REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 10 | 2020

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Metals in waste waters

Mirja Leivuori, Riitta Koivikko, Timo Sara-Aho Teemu Näykki, Keijo Tervonen, Sari Lanteri, Ritva Väisänen and Markku Ilmakunnas

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ABSTRACT

Interlaboratory Proficiency Test 11/2019

Proftest SYKE carried out the proficiency test (PT) for analysis of elements in waste waters in October-November 2019 (MET 11/19). The measurands for the synthetic and waste water samples were: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, V, and Zn. In total 23 laboratories participated in the PT.

In total, 89 % of the results evaluated with z scores were satisfactory when total deviation of 10–25 % from the assigned value was accepted. Of the results evaluated with E_n scores, 91 % were satisfactory. Basically, either the metrologically traceable concentration, the calculated concentration, the robust mean, the mean or the median of the results reported by the participants was used as the assigned value for measurands.
Warm thanks to all the participants in this proficiency test!

Keywords: water analysis, metals, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, V, Zn, water and environmental laboratories, proficiency test, interlaboratory comparison

TIIVISTELMÄ

Laboratorioiden välinen pätevyyskoe 11/2019

Proftest SYKE järjesti loka-marraskuussa 2019 pätevyyskokeen laboratorioille, jotka määrittävät metalleja ja elohopeaa jätevesistä (MET 11/2019). Pätevyyskokeessa määritettiin synteettisestä sekä jätevesinäytteistä testisuureet Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, V ja Zn. Pätevyyskokeeseen osallistui yhteensä 23 laboratoriota.

Koko aineistossa oli 89 % hyväksyttäviä tuloksia z-arvoilla arvioituja, kun tulosten sallittiin poiketa vertailuarvosta 10–25 %. Tuloksista, jotka arvioitiin E_n-arvoilla, hyväksyttyjä oli 91 %. Testisuureen vertailuarvona käytettiin metrologisesti jäljitettävää pitoisuutta, laskennallista pitoisuutta, osallistujien ilmoittamien tulosten robustia keskiarvoa, keskiarvoa tai mediaania.
Kiitos pätevyyskokeen osallistujille!

Avainsanat: vesianalyysi, metallit, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, V, Zn, vesi- ja ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus

SAMMANDRAG

Provningsjämförelse 11/2019

Proftest SYKE genomförde en provningsjämförelse i oktober-november 2019 (MET 11/19), som omfattade bestämningen av Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, V och Zn i syntetiska provet och avloppsvatten. Tillsammans 23 laboratorier deltog i jämförelsen.

I jämförelsen 89 % av resultaten som värderades med hjälp z värdet var acceptabla, när total deviation på 10–25 % från referensvärdet tillåten. Resultaten som värderades med hjälp E_n värdet var 91 % acceptabla. Som referensvärde av analytens koncentration användes mest det metrologiska spårbara värdet, teoretiska värdet eller robust medelvärdet, medelvärdet eller median av deltagarnas resultat.
Ett varmt tack till alla deltagarna i testet!

Nyckelord: vattenanalyser, metaller, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, V, Zn, provningsjämförelse, vatten- och miljölaboratorier

CONTENTS

1 Introduction

Proftest SYKE carried out a proficiency test (PT) for analysis of metals and mercury in different kinds of waste waters in October - November 2019 (MET 11/2019). The measurands for the synthetic sample and waste water samples were: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, V, and Zn. In the PT the results of Finnish laboratories providing environmental data for Finnish environmental authorities were evaluated. Additionally, other water and environmental laboratories were welcomed to participate in the proficiency test.

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international standard ISO/IEC 17043 [1] and applying ISO 13528 [2] and IUPAC Technical report [3]. Proftest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope of the Proftest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer

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The responsibilities in organizing the proficiency test

Mirja Leivuori	coordinator
Riitta Koivikko	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance
Ritva Väisänen	technical assistance

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Timo Sara-Aho, SYKE (metals, ID-ICP-MS),
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2.2 Participants

In total 23 laboratories participated in this proficiency test (Appendix 1), 22 participants from Finland and one from another European country. One participant reported two sets of results. Altogether 50 % of the participants used accredited analytical methods at least for a part of the measurements. For this proficiency test, the organizing laboratory has the code 23 (SYKE, Helsinki, T003, www.finas.fi/sites/en) in the result tables.

2.3 Samples and delivery

Four types of samples were delivered to the participants: synthetic sample as well as paper and pulp industrial, municipal and industrial waste water samples. The synthetic sample A1M was prepared from the NIST traceable commercial reference material produced by Inorganic Ventures. The synthetic sample A1Hg was prepared by diluting from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc. The sample preparation is described in detail in the Appendix 2. The synthetic sample A1M was acidified with nitric acid and the synthetic mercury sample A1Hg with the hydrochloric acid.

The paper and pulp industrial waste water samples P2M and P2Hg (for Hg measurements) were prepared with additions of single element standard solutions (AccuStandard for Hg and Merck CertiPUR® for other elements, Appendix 2). The industrial waste water samples T3M (after analysis: TN3 – no digestion / TY3 – digestion with acid or with acid mixture) and T3Hg for Hg measurements were prepared with additions of the same single element standard solutions as the samples P2M and P2Hg. The municipal waste water samples V4M and V4Hg were prepared with additions of the same single element standard solutions (Appendix 2).

When preparing the samples, the purity of the used sample vessels was controlled. The randomly chosen sample vessels were filled with deionized water and the purity of the sample vessels was controlled after 3 days by analyzing Cd, Cu, Hg, and Zn. According to the test results all used vessels fulfilled the purity requirements.

The samples were delivered to the participants abroad on 7 October 2019 and on 8 October 2019 to the national participants. The samples arrived at the participants mainly on 10 October 2019. Two participants reported the samples arrival on 15 October at the latest. However, they also reported within-laboratory delivery problems.

The samples were requested to be measured as follows:

Hg samples	latest on 18 October 2019
Other samples	latest on 1 November 2019

The results were requested to be reported latest on 1 November 2019. The participants delivered the results accordingly. The preliminary results were delivered to the participants via ProftestWEB and email on 13 November 2019.

2.4 Homogeneity and stability studies

The homogeneity of the samples was tested by analyzing Cd, Cr, Cu, Hg, Pb, Se, Ti, and Zn. More detailed information of homogeneity study is shown in Appendix 3. According to the homogeneity test results, all samples were considered homogenous. The synthetic samples were prepared from traceable certified reference materials, and thus known to be homogenous. However, homogeneity of these was checked by three measurements of two samples and they were considered homogenous. Based on the earlier similar proficiency tests the water samples are known to be stable over the given time period for the test.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 4. The comments from the participants mainly dealt with the delivery delays and their result reporting errors. The comment from the provider is for the missing sample arrival document. All the feedback is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

To test the normality of the data the Kolmogorov-Smirnov test was applied. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. The results which differed from the data more than $5 \times s_{rob}$ or 50 % from the robust mean were rejected before the statistical results handling.

If the result has been reported as below detection limit, it has not been included in the statistical calculations. More information about the statistical handling of the data is available from the Guide for participant [4].

2.6.2 Assigned values

For the synthetic sample A1M the NIST traceable calculated concentrations were used as the assigned value, with exception of Pb and Hg. The results based on isotope dilution (ID) ICP-MS technique were used as the assigned value for Hg and Pb in samples A1M, P2M, TN3, V4M, A1Hg, P2Hg and T3Hg. The assigned value based on the ID-ICP-MS method is the mean of the homogeneity results and the test result (9 or 12 results). The ID-ICP-MS method is accredited for soluble lead and mercury in synthetic sample and natural as well as waste waters in the scope of calibration laboratory (K054; www.finas.fi/sites/en). For the other samples and measurands the robust mean was used as the assigned value. When the number of results was low, the mean or the median was used as the assigned value ($n_{stat}<12$).

The robust mean, the mean and the median are not metrologically traceable assigned values. As it was not possible to have metrologically traceable assigned values for all measurands, in those cases the robust mean, the mean or the median of the results was the best available value to be used as the assigned value. The reliability of the assigned value was statistically tested [1, 2].

The expanded uncertainty for the calculated assigned values ($k=2$) was estimated using standard uncertainties associated with individual operations involved in the preparation of the sample. The main individual source of the uncertainty was the uncertainty of the concentration in the stock solution.

When the robust mean, the mean or the median was used as the assigned value, the uncertainty was calculated using the robust standard deviation or standard deviation, respectively [1, 2, 4]. For the metrologically traceable mercury and lead results, the uncertainty is the expanded measurement uncertainty of the ID-ICP-MS method.

The expanded uncertainty of the calculated and metrologically traceable assigned values for metals in the synthetic samples varied between 0.4 and 3 %. When using the robust mean, the mean or the median of the participant results as the assigned value, the expanded uncertainties of the assigned values were between 1.3 and 19 % (Appendix 5).

The assigned values **have not been changed** after reporting the preliminary results.

2.6.3 Standard deviation for proficiency assessment and results' evaluation

The results of this proficiency test were evaluated both with the z and E_n scores.

The standard deviation for proficiency assessment was estimated based on the uncertainty of the assigned value, the concentration of the measurand, the results of homogeneity and stability tests, and the long-term variation in the former proficiency tests. The standard deviation for the proficiency assessment ($2\times s_{pt}$, at the 95 % confidence interval) was set to 10–25 % depending on the measurement. The results of Sb of the sample TY3 are not evaluated, but the assigned value is given as the median of the results. The results of mercury in the sample V4Hg are evaluated only with E_n scores due to the high variation between the results.

The performance evaluation by means of the E_n scores ('*Error, normalized*') used the assigned value based on the participants' results and the uncertainty of the assigned value. E_n scores are used to evaluate the difference between the assigned value and participant's result within their claimed expanded uncertainty. E_n scores are calculated:

$$(E_n)_i = \frac{x_i - x_{pt}}{\sqrt{U_i^2 + U_{pt}^2}}, \text{ where}$$

x_i = participant's result, x_{pt} = assigned value, U_i = the expanded uncertainty of a participant's result and U_{pt} = the expanded uncertainty of the assigned value.

Scores of E_n $-1.0 < E_n < 1.0$ should be taken as an indicator of successful performance when the uncertainties are valid. Whereas scores $E_n \geq 1.0$ or $E_n \leq -1.0$ could indicate a need to review the uncertainty estimates, or to correct a measurement issue.

After reporting the preliminary results no changes have been done for the standard deviations of the proficiency assessment values.

When using the robust mean, the median or the mean as the assigned value, the reliability was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where u_{pt} is the standard uncertainty of the assigned value and s_{pt} is the standard deviation for proficiency assessment [3]. When testing the reliability of the assigned value the criterion was mainly fulfilled and the assigned values were considered reliable.

The reliability of the standard deviation and the corresponding z score was estimated by comparing the deviation for proficiency assessment (s_{pt}) with the robust standard deviation (s_{rob}) or standard deviation (s, $n_{stat} < 12$) of the reported results (the criteria) [3]. The criterion $s_{rob} / s_{pt} < 1.2$ was mainly fulfilled.

In the following cases, the criterion for the reliability of the assigned value[1] and/or for the reliability of the standard deviation for proficiency assessment[2] was not met and, therefore, the evaluation of the performance is weakened in this proficiency test:

Sample	Measurand
P2M	Ti[1], Zn[1,2], Sr[1]
TN3	Co[1]
TY3	Co[1], Cr[1,2], Cu[1], Mg[1]
V4M	Cu[1], Se[1,2]

3 Results and conclusions

3.1 Results

The terms in the results table are explained in the Appendix 6. The results and the performance of each participant are presented in Appendix 7 and the summary of the results in Table 1. The summaries of the z and E_n scores are shown in Appendices 8 and 9. In Appendix 10 the z scores are shown in the ascending order. The reported results grouped by the used analytical methods with their expanded uncertainties (k=2) are presented in Appendix 11.

The robust standard deviations of the results varied from 2.6 % to 28 % and the standard deviations varied from 0.1 % to 18 % (Table 1). The robust standard deviation or the standard deviation of results was lower than 10 % for 69 % and for 74 % of the results, respectively. The robust standard deviations for waste water samples were approximately in the same range as in the previous similar proficiency test MET 10/2018, where the deviations varied from 2.8 % to 20 % [5].

Table 1. The summary of the results in the proficiency test MET 11/2019.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob} / s	s_{rob} % / s %	2 x s_{pt} %	n_{all}	Acc z % / E_n %
Al	A1M	µg/l	115	112	117	112	24	20.3	15	17	59
	P2M	µg/l	202	199	199	202	25	12.8	20	11	82
	TN3	µg/l	79.2	79.3	79.1	79.2	8.0	10.1	20	13	85
	TY3	µg/l	96.0	94.4	94.4	96.0	16.3	17.3	25	7	100
	V4M	µg/l	110	110	108	110	13	11.9	20	12	83
As	A1M	µg/l	55.0	53.0	52.8	53.2	2.7	5.1	10	13	92
	P2M	µg/l	11.2	11.1	11.1	11.2	1.2	10.6	20	11	82
	TN3	µg/l	50.2	50.3	50.2	48.9	4.1	8.1	20	14	93
	TY3	µg/l	52.7	52.1	-	52.7	*4.8*	*9.3*	-	5	*- / 100*
	V4M	µg/l	5.35	5.34	5.34	5.35	0.37	7.0	20	12	83
B	A1M	µg/l	85.0	80.4	80.0	81.2	6.3	7.9	10	12	45
	P2M	µg/l	68.9	67.2	67.2	68.9	4.6	6.9	20	11	70
	TN3	µg/l	157	158	158	157	21	13.6	25	11	82
	TY3	µg/l	198	196	-	198	*6.0*	*3.3*	-	4	*- / 100*
	V4M	µg/l	93.5	93.5	93.3	92.9	7.8	8.4	20	12	91
Ba	A1M	µg/l	130	122	122	121	7	5.8	10	11	82
	P2M	µg/l	198	198	198	200	16	8.1	15	10	90
	TN3	µg/l	74.2	75.1	75.1	74.2	7.4	9.8	15	10	90
	TY3	µg/l	78.3	78.5	-	78.3	*5.8*	*7.4*	-	4	*- / 100*
	V4M	µg/l	62.4	62.5	62.5	62.4	5.6	9.0	15	10	100
Ca	A1M	mg/l	33.0	32.7	32.9	32.8	1.0	3.1	10	15	93
	P2M	mg/l	63.8	63.8	63.9	63.8	3.3	5.2	10	11	100
	TN3	mg/l	65.5	65.4	65.5	65.8	1.9	2.9	10	15	100
	TY3	mg/l	65.6	66.7	-	65.6	*3.1*	*4.6*	-	3	*- / 100*
	V4M	mg/l	33.9	34.0	33.9	34.0	0.9	2.6	10	12	100
Cd	A1M	µg/l	4.50	4.43	4.43	4.47	0.22	5.0	15	13	100
	P2M	µg/l	2.00	2.00	2.01	2.00	0.12	5.9	15	11	100
	TN3	µg/l	9.96	9.96	9.96	10.00	0.56	5.7	15	13	100
	TY3	µg/l	10.7	10.8	-	10.7	*0.90*	*8.2*	20	6	100
	V4M	µg/l	6.96	6.93	6.96	7.08	0.40	5.8	15	12	100
Co	A1M	µg/l	11.0	10.4	10.4	10.5	0.7	6.3	15	16	94
	P2M	µg/l	14.0	14.2	14.2	14.0	1.5	10.6	20	11	91
	TN3	µg/l	10.1	10.1	10.1	10.0	1.0	10.4	20	14	79
	TY3	µg/l	10.7	11.0	-	10.7	*1.0*	*9.3*	20	6	100
	V4M	µg/l	5.04	5.04	4.97	4.97	0.27	5.4	20	12	83
Cr	A1M	µg/l	15.0	14.7	14.6	14.5	1.3	8.8	15	18	89
	P2M	µg/l	4.64	4.73	4.71	4.64	0.41	8.6	15	11	91
	TN3	µg/l	13.4	13.5	13.4	13.5	1.1	8.4	20	15	93
	TY3	µg/l	13.1	13.9	13.9	13.1	2.4	17.6	25	7	86
	V4M	µg/l	7.82	7.82	7.82	7.73	0.63	8.1	15	12	100
Cu	A1M	µg/l	33.0	31.6	31.6	31.6	1.4	4.5	10	18	89
	P2M	µg/l	21.1	21.2	21.1	21.0	1.7	8.1	20	13	100
	TN3	µg/l	18.1	18.1	18.1	17.5	2.1	11.5	25	15	100
	TY3	µg/l	16.3	16.8	-	16.3	*2.0*	*11.9*	25	6	83
	V4M	µg/l	3.05	3.1	3.1	3.0	0.4	12.9	25	14	92

Table 1. The summary of the results in the proficiency test MET 11/2019.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob} / s	s_{rob} % / s %	2 x s_{pt} %	n_{all}	Acc z % / E_n %
Fe	A1M	µg/l	230	223	223	223	13	5.6	10	22	82
	P2M	µg/l	84.9	83.9	83.9	84.9	12.5	14.8	25	13	85
	TN3	µg/l	159	159	159	159	11	6.7	15	19	89
	TY3	µg/l	154	158	-	154	*11*	*6.7*	-	6	*- / 100*
	V4M	µg/l	44.1	44.3	44.1	43.8	2.6	5.8	15	13	85
Hg	A1Hg	µg/l	0.84	0.85	0.85	0.83	0.11	13.3	20	14	79
	P2Hg	µg/l	0.44	0.46	0.45	0.44	0.06	12.8	20	12	75
	T3Hg	µg/l	3.47	3.43	3.44	3.39	0.32	9.3	20	14	93
	V4Hg	µg/l	2.29	2.10	2.10	2.29	0.59	28.1	-	12	*- / 40*
K	A1M	mg/l	25.0	24.3	24.3	24.3	0.7	2.9	10	12	100
	P2M	mg/l	36.1	36.1	36.3	36.0	1.5	4.1	10	11	91
	TN3	mg/l	43.8	43.8	44.0	43.6	1.4	3.1	10	11	91
	TY3	mg/l	43.1	43.5	-	43.1	*1.9*	*4.3*	-	4	*- /100*
	V4M	mg/l	21.8	21.8	21.8	22.0	0.7	3.2	10	12	100
Mg	A1M	mg/l	13.5	13.2	13.2	13.2	0.4	3.0	10	17	100
	P2M	mg/l	11.9	11.8	11.9	11.9	0.3	2.6	10	11	91
	TN3	mg/l	19.7	19.6	19.7	19.6	0.8	3.8	10	14	100
	TY3	mg/l	19.3	19.9	-	19.3	*1.3*	*6.4*	15	6	83
	V4M	mg/l	7.49	7.49	7.49	7.52	0.31	4.1	10	12	100
Mn	A1M	µg/l	45.9	44.6	44.6	44.4	3.3	7.4	10	17	88
	P2M	µg/l	18.0	18.4	18.4	18.0	2.5	13.5	20	11	100
	TN3	µg/l	169	169	169	172	13	7.9	15	16	100
	TY3	µg/l	165	169	-	165	*10*	*5.8*	-	4	-
	V4M	µg/l	68.7	68.7	68.7	68.2	5.7	8.3	20	12	100
Mo	A1M	µg/l	22.5	22.4	22.5	22.4	1.1	5.0	10	15	87
	P2M	µg/l	6.20	6.18	6.18	6.20	0.73	11.8	20	12	83
	TN3	µg/l	1202	1202	1201	1181	61	5.1	10	15	73
	TY3	µg/l	1246	1246	-	1246	*107*	*8.6*	-	3	*- / 67*
	V4M	µg/l	12.3	12.6	12.6	12.3	1.4	11.4	20	12	75
Ni	A1M	µg/l	17.5	16.9	16.9	17.0	1.2	6.8	10	16	81
	P2M	µg/l	10.5	10.8	10.8	10.5	1.0	9.5	15	11	91
	TN3	µg/l	28.1	28.1	28.1	28.0	2.6	9.2	15	15	100
	TY3	µg/l	27.8	29.3	-	27.8	*5.2*	*17.7*	-	4	*- / 75*
	V4M	µg/l	6.00	6.01	6.01	6.00	0.43	7.2	15	13	92
Pb	A1M	µg/l	18.8	17.3	17.5	17.6	1.7	9.6	10	13	69
	P2M	µg/l	10.0	9	9	9	2	17.0	15	11	64
	TN3	µg/l	30.5	27.8	27.8	27.4	3.3	11.8	15	12	75
	TY3	µg/l	28.9	28.6	-	28.9	*3.3*	*11.8*	20	6	100
	V4M	µg/l	3.15	2.78	2.80	2.79	0.40	14.3	20	12	67
Sb	A1M	µg/l	33.0	31.7	31.8	31.7	2.2	6.9	10	12	83
	P2M	µg/l	25.5	25.6	25.5	25.5	1.9	7.4	15	11	100
	TN3	µg/l	9.2	9.2	9.2	8.9	1.1	12.4	20	12	100
	TY3	µg/l	7.82	7.96	-	7.82	*0.51*	*6.4*	-	4	-
	V4M	µg/l	13.2	12.8	12.9	13.2	1.4	10.6	20	11	91

Table 1. The summary of the results in the proficiency test MET 11/2019.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob} / s	s_{rob} % / s %	2 x s_{pt} %	n_{all}	Acc z % / E_n %
Se	A1M	µg/l	18.5	18.6	18.7	18.5	1.2	6.4	10	12	83
	P2M	µg/l	35.1	35.1	34.9	35.6	3.4	9.7	20	11	100
	TN3	µg/l	13.9	13.9	13.9	13.6	1.4	10.0	20	11	100
	TY3	µg/l	15.3	14.8	-	15.3	*2.4*	*16.5*	-	4	*- / 100*
	V4M	µg/l	19.8	19.4	19.5	19.8	1.8	9.2	15	11	91
Sn	A1M	µg/l	17.5	16.8	16.8	16.9	1.0	5.7	10	11	91
	P2M	µg/l	8.03	8.03	8.25	8.00	1.32	16.1	25	10	90
	TN3	µg/l	33.6	33.6	33.6	32.8	2.6	7.7	15	10	100
	TY3	µg/l	33.9	33.6	-	33.9	*1.7*	*4.9*	-	4	*- / 100*
	V4M	µg/l	0.72	0.76	0.76	0.72	0.21	28.0	-	10	- / 100
Sr	A1M	µg/l	110	106	107	106	2	2.3	10	11	73
	P2M	µg/l	200	199	203	200	22	10.6	15	9	89
	TN3	µg/l	150	148	147	150	9	6.2	15	10	100
	TY3	µg/l	150	150	-	150	*0.2*	*0.1*	-	4	*- / 100*
	V4M	µg/l	79.2	80.7	80.5	79.2	3.6	4.5	10	10	90
Ti	A1M	µg/l	35.5	35.2	35.2	35.4	1.9	5.3	10	10	100
	P2M	µg/l	16.0	16.2	16.2	16.0	2.4	14.8	25	10	89
	TN3	µg/l	116	116	116	116	5	4.2	10	10	100
	TY3	µg/l	125	123	-	125	*5.0*	*4.0*	-	3	*- / 100*
	V4M	µg/l	50.1	49.9	49.9	50.1	2.1	4.2	10	10	100
V	A1M	µg/l	13.5	13.3	13.2	13.1	0.7	5.3	10	10	90
	P2M	µg/l	6.19	6.35	6.30	6.19	0.48	7.6	20	10	90
	TN3	µg/l	132	132	133	132	6	4.4	15	10	90
	TY3	µg/l	138	142	-	138	*14*	*9.8*	-	3	*- / 100*
	V4M	µg/l	34.6	34.3	34.3	34.6	1.7	4.8	15	10	100
Zn	A1M	µg/l	54.5	54.7	54.6	53.9	4.4	8.2	10	21	71
	P2M	µg/l	21.3	21.4	21.3	20.4	2.8	13.1	20	13	92
	TN3	µg/l	170	169	170	173	12	7.3	15	19	89
	TY3	µg/l	171	167	-	171	*24*	*14.6*	-	7	*- / 83*
	V4M	µg/l	42.5	42.6	42.5	42.4	1.9	4.5	15	14	100

Rob. mean: the robust mean, s_{rob}: the robust standard deviation, *s: standard deviation*, s_{rob} %: the robust standard deviation as percent, *s %: standard deviation as percent*, $2 \times s_{pt}$ %: the standard deviation for proficiency assessment at the 95 % confidence level, n_{all}: the total number of the participants, Acc z %: the results (%), where $|z| \leq 2$, *Acc E_n %: the results, where* $|E_n| < 1$.

3.2 Analytical methods

The participants could use different analytical methods for the measurements in the PT. The used analytical methods and results of the participants grouped by methods are shown in more detail in Appendix 11. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5. The statistically significant differences are shown in Appendix 12.

Effect of sample pretreatment on elemental concentrations in waste waters

Elements in waste water were mainly measured from acidified samples without sample pretreatment except for the industrial waste water sample (TN3/TY3). The participants measured the acidified industrial waste water mostly without sample pretreatment (TN3), and a smaller

part of the participants measured the industrial waste water after acid digestion (TY3). The results of these samples were evaluated separately (Table 1).

The difference between the average concentrations of elements measured by different sample pretreatment methods was tested using the t-test. Statistically significant difference was observed for aluminium and cadmium analyses. For these measurands no pretreatment approach gave statistically significantly lower results compared to the pretreatment with acid digestion (Appendix 12). For an unfiltered waste water sample the results are expected, acid digestion should give similar or higher results than without digestion.

Effect of measurement methods on elemental results
The most commonly used analytical method was mainly ICP-MS, followed by ICP-OES. FAAS or GAAS technique was used by one participant for some measurements. Hydride generation ICP-OES and AAS techniques were both used by one participant for some measurements (Appendix 11).

The difference between the average concentrations of metals measured by different measurement methods was tested using the t-test. Statistically significant differences were noticed for aluminium in the sample TN3, where ICP-OES technique gave lower results than ICP-MS technique (Appendix 12).

As a general note, a low recovery may be an indication of loss of measurand which can occur during sample pretreatment (e.g. volatilization during acid digestion) or measurement (e.g. GAAS analysis). It may also be caused by incorrect background correction (ICP-OES) or matrix effects.

Recoveries that are too high may be caused by spectral interferences (overlapping wavelengths in emission spectrometry, polyatomic or isobaric interferences in mass spectrometry), matrix effects or contamination.

Matrix effects can often be overcome by matrix matching the calibration standards, however this is often difficult with environmental samples since the elemental concentrations vary a lot even within the same sample type.

Effect of measurement methods on mercury results
For the analysis of mercury, ICP-MS was the most often used method of analysis. That was followed by CV-AFS. Also, some participants (1-3) reported to measure mercury with CV-AAS, CV-ICP-OES and CV-ICP-MS techniques (Appendix 11).

Analytical techniques do not have so much effect on the results, but the fact is that for example using CV-AFS lower detection limits can be achieved compared to CV-AAS. CV-ICP-MS technique is known to have very competent detection limits as well.

3.3 Uncertainties of the results

At maximum 70 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 2, Appendix 11). Several approaches were used for

estimating the measurement uncertainty (Appendix 13). The most commonly used approach was based on the method validation data or using the internal quality data in different ways [6]. MUkit measurement uncertainty software for the estimation of the uncertainties was used by at maximum three participants (Appendix 13) [7]. The free software is available on the webpage: www.syke.fi/envical/en. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

The range of the reported uncertainties varied between the measurements and the sample types. As can be seen in Table 2, some of the participants have over-estimated their expanded ($k=2$) measurement uncertainty. In this proficiency test several high measurement uncertainties were reported, i.e. 50 % or higher, marked as bold in Table 2. Further, n this PT very high measurement uncertainties (up to 100 %) were reported more than in the previous similar PT Proftest SYKE MET 10/2018 [5]. Very high measurement uncertainties should not exist, unless the measured concentration is near to the limit of quantification.

In order to promote the enhancement of environmental measurements' quality standards and traceability, the national quality recommendations for data included into water quality registers have been published in Finland [8]. The recommendations for measurement uncertainties for most of the tested measurands in waste water are 20 %. In this proficiency test some of the participants had their measurement uncertainties within these limits, while some did not achieve them. Harmonization of the uncertainty's estimation should be continued.

Table 2. The range of the expanded measurement uncertainties ($k=2$, U_i%) reported by the participants.

Measurand	A1M/A1Hg %	P2M/P2Hg %	TN3/T3Hg %	TY3 %	V4M/V4Hg %
Al	5-40	10-40	5-40	8-25	5-40
As	4-25	10-25	4-25	10-25	10-30
B	12-**100**	12-**100**	6-**50**	20	12-**100**
Ba	10-20	10-20	10-17	10-20	10-**20**
Ca	5-20	6-20	5-20	6-15	5-20
Cd	10-**60**	10-33	10-**50**	15-33	10-**50**
Co	9-**100**	9-20	10-**100**	14-20	9-**100**
Cr	9-**50**	10-30	9-**50**	14-20	10-**50**
Cu	10-40	10-40	10-40	15-34	**10-100**
Fe	5-40	10-40	5-40	13-33	10-40
Hg	12-46	15-46	12-40	-	12-40
K	5-23	10-23	5-23	12-23	5-23
Mg	5-20	10-20	5-20	7-20	5-20
Mn	8-40	8-40	5-20	9-18	7-40
Mo	5-40	10-40	5-20	12-15	10-40
Ni	9-**80**	10-20	9-**50**	14-17	10-**100**
Pb	10-20	10-30	10-**100**	12-25	10-30
Sb	10-26	10-26	10-26	15-30	10-30
Se	12-30	12-29	15-29	20-30	12-30
Sn	10-25	10-30	15-25	15-25	15-**80**
Sr	9-25	9-25	8-25	15-25	9-25
Ti	15-**100**	15-**100**	10-**50**	10-15	10-**100**
V	10-20	10-30	10-20	13-15	10-20
Zn	10-40	10-40	10-29	10-29	10-40

4 Evaluation of the results

The performance evaluation of the participants was based on the z and E_n scores, which were calculated using the assigned values and the standard deviation for the performance assessment. The z and E_n scores were interpreted as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory
$-1.0 < E_n < 1.0$	Satisfactory
$E_n \leq -1.0$ or $E_n \geq 1.0$	Unsatisfactory

In total, 89 % of the results evaluated with z scores were satisfactory when total deviation of 10–25 % from the assigned value was accepted (Appendix 8). Of the results evaluated with E_n scores, 91 % were satisfactory (Appendix 9).

Altogether 50 % of the participants used accredited analytical methods at least for a part of the measurements and 91 % of their results were satisfactory. The summary of the performance evaluation and comparison to the previous similar PT is presented in Table 3. In the previous similar PT, Proftest SYKE MET 10/2018, the performance was satisfactory for 84 % of the participants result of waste waters when standard deviation of 10–25 % from the assigned values was accepted [5].

In general, the share of satisfactory results varied between 84 % and 93 %, based on evaluation with z scores, for the tested sample types (Table 3). In total the share was at the same level as in the previous similar proficiency test in 2018 (Table 3) [5]. The share of satisfactory results in the synthetic sample A1M was the lowest for B, about 45 %.

For the paper and pulp industrial waste water sample P2M the share of satisfactory results varied between 70 % (B) and 100 % (Ca, Cd, Cu, Mn, Sb, and Se). In total 90 % of the results in the sample P2M and 75 % in the sample P2Hg were satisfactory, when accepting the deviation of 10-25 % from the assigned value (Table 3).

Table 3. Summary of the performance evaluation in the proficiency test MET 11/2019.

Sample	Satisfactory results (mean, %)	Accepted deviation from the assigned value (%)	Remarks
A1M / A1Hg	84 / 79	10-20	- Difficulties in measurements for Al, B, Pb, Sr, Zn, < 80% satisfactory results. - In the MET 10/2018 the performance was satisfactory for 91/80 % of the results [5].
P2M / P2Hg	90 / 75	10-25	- Somewhat approximate assessment for: Ti, Zn, Sr. - Mainly good performance in the sample P2M. - Difficulties in measurements for B, Hg, Pb, < 80% satisfactory results.
TN3 / T3Hg	93 / 93	10-25	- Somewhat approximate performance evaluation for Co. - Mainly good performance. - Difficulties in measurements for Co, Mo, Pb < 80% satisfactory results. - In the MET 10/2018 the performance was satisfactory for 95 / 80% of the results [5].
TY3	z score: 93 E_n score: 91	15-25	- Somewhat approximate performance evaluation for Co, Cr, Cu, Mg. - Many results were evaluated based on E_n scores due to low number of results. - In the MET 10/2018 the performance was satisfactory based on z scores for 74 % of the results when accepting deviation of 10-20 % from the assigned value and based on E_n scores 64 % [5].
V4M / V4Hg	92 / E_n 40	10-25	- Somewhat approximate performance evaluation for Cu, Se. - Mainly good performance in the sample P2M. - Difficulties in measurements for Mo, Pb < 80% satisfactory results. - Hg results were evaluated based on E_n scores due to due to the high variation between the results. - In the MET 10/2018 the performance was satisfactory based on z score evaluation for 86 / 85 % of the results [5].

For the industrial waste water sample (TN3, no digestion and T3Hg) 93 % of the results were satisfactory, when deviation of 10–25 % from the assigned value was accepted (Table 3). For Ca, Cd, Cu, Mg, Mn, Ni, Sb, Se, Sn, Sr, and Ti in the sample TN3 all the results were satisfactory. For the industrial waste water sample digested with acid or with acid mixture, TY3, the performance evaluation was done with z and E_n scores. For both, the performance was better than in the previous similar PT, Proftest SYKE MET 10/2018 (Table 3) [5].

For the municipal waste water samples V4M the performance evaluation was done mainly with z scores and for V4Hg with E_n scores. The number of satisfactory results evaluated based on z scores was almost in the same level than in the previous similar PT Proftest SYKE MET 10/2018 (Table 3) [5]. For Ba, Ca, Cd, Cr, K, Mg, Mn, Ti, V and Zn in the sample V2M all the results were satisfactory.

5 Summary

Proftest SYKE carried out the proficiency test (PT) for analysis of elements in waste waters in October - November 2019 (MET 11/2019). The measurands for the synthetic sample and waste water samples were: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, V, and Zn. In total 23 laboratories participated in the PT.

The calculated concentration (the NIST traceable) or the robust mean, the mean or the median of the results reported by the participants was chosen to be the assigned value for the measurand, with the exception of Pb and Hg where the used assigned values were based on the metrologically traceable isotope dilution (ID) ICP-MS technique for some samples. The uncertainty for the assigned value was estimated at the 95 % confidence level ($k=2$) and it was between 0.4 and 3 % for the calculated and metrologically traceable assigned values and for assigned values based on the robust mean, the mean or the median it was between 1.3 and 19 %.

The evaluation of the performance was based on the z or E_n scores. In total, 89 % of the results evaluated with z scores were satisfactory when total deviation of 10–25 % from the assigned value was accepted. Of the results evaluated with E_n scores, 91 % were satisfactory. Altogether 50 % of the participants used accredited analytical methods at least for a part of the measurements and 91 % of their results were satisfactory.

6 Summary in Finnish

Proftest SYKE järjesti loka-marraskuussa 2019 pätevyyskokeen laboratorioille, jotka määrittävät metalleja ja elohopeaa erityyppisistä jätevesistä (MET 11/2019). Pätevyyskokeessa määritettiin synteettisestä sekä jätevesinäytteistä testisuureet Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Ti, V ja Zn. Pätevyyskokeeseen osallistui yhteensä 23 laboratoriota.

Testisuureen vertailuarvona käytettiin laskennallista pitoisuutta tai osallistujien tulosten robustia keskiarvoa, keskiarvoa tai mediaania. Lyijylle ja elohopealle käytettiin metrologisesti jäljitettävää vertailuarvoa osassa testinäytteistä. Vertailuarvolle laskettiin epävarmuus 95 % luottamusvälillä. Vertailuarvon laajennettu epävarmuus oli 0,4 – 3 % laskennallista tai metrologisesti jäljitettävää pitoisuutta vertailuarvona käytettäessä ja muilla välillä 1,3 – 19 %.

Pätevyyden arviointi tehtiin z- tai E_n-arvojen avulla. Koko aineistossa hyväksyttäviä z-arvoilla arvioituja tuloksia oli 89 %, kun tulosten sallittiin poiketa vertailuarvosta 10 – 25 %. Tuloksista, jotka arvioitiin E_n-arvoilla, hyväksyttyjä oli 91 %. Noin 50 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 91 %.

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APPENDIX 1: Participants in the proficiency test

Country	Participant
Finland	Boliden Harjavalta Oy Boliden Kokkola Oy Eurofins Ahma Oy, Oulu Eurofins Environment Testing Finland Oy, Lahti Freeport Cobalt Oy Hortilab Ab Oy KVVY Tutkimus Oy, Tampere Kymen Ympäristölaboratorio Oy Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku MetropoliLab Oy Neste Corporation, Technology Center, Kilpilahti Norilsk Nickel Harjavalta Oy Outokumpu Stainless Oy, Tutkimuskeskus, Tornio Pyhäsalmi Mine Oy SGS Finland Oy, Kotka SSAB Europe Oy, Analyysilaboratorio, Hämeenlinna SSAB Europe Raahe, Raahe SYKE, Helsingin toimipaikka SYNLAB Analytics & Services Finland Oy UPM Tutkimuskeskus, Lappeenranta Venator, Pori Yara Suomi Oy, Siilinjärvi
Norway	Eurofins Environment Norway A/S, Moss, Norway

APPENDIX 2: Sample preparation

The synthetic sample A1M was prepared by diluting from the NIST traceable certified reference materials produced by Inorganic Ventures. The synthetic sample A1Hg was prepared by diluting from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc. The waste water samples P2M, T3M and V4M were prepared by adding some separate metal solutions (Merck CertiPUR®) into the original water sample, if the original concentration was not high enough. Samples P2Hg, T3Hg and V4Hg were prepared by adding from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc., if the original concentration was not high enough.

Measurand		A1M µg/l	P2M µg/l	TN3/ TY3, µg/l	V4M µg/l	Measurand		A1M µg/l	P2M µg/l	TN3/ TY3, µg/l	V4M µg/l
Al	Original	1 150	200	73	5.6	**K**	Original	250 000	37 000	45 000	23 000
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	-	-	100		Addition	-	-	-	-
	Ass. value	115	202	79.2/96.0	110		Ass. value	25 000	36 100	43 800/ 43 100	21 800
As	Original	550	0.38	0.84	0.18	**Mg**	Original	135 000	12 000	20 000	7 900
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	10	50	5		Addition	-	-	-	-
	Ass. value	55.0	11.2	50.2/52.7	5.35		Ass. value	13 500	11 900	19 700/ 19 300	7 490
B	Original	850	73	160	99	**Mn**	Original	459	18	170	21
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	-	-	-		Addition	-	-	-	50
	Ass. value	85.0	68.9	157/198	93.5		Ass. value	45.9	18.0	169/165	68.7
Ba	Original	1 300	180	63	3.5	**Mo**	Original	225	5.8	1 300	5.2
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	-	-	50		Addition	-	-	-	10
	Ass. value	130	198	74.2/78.3	62.4		Ass. value	22.5	6.20	1 202/ 1 246	12.3
Ca	Original	330 000	65 000	67 000	35 000	**Ni**	Original	175	1.4	27	6.4
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	-	-	-		Addition	-	10	-	-
	Ass. value	33 000	63 800	65 500/ 65 600	33 900		Ass. value	17.5	10.5	28.1/27.8	6.00
Cd	Original	45	0.05	0.34	0.01	**Pb**	Original	189	0.2	0.12	0.09
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	2	10	7		Addition	-	10	30	3
	Ass. value	4.50	2.00	9.96/10.7	6.96		Ass. value	18.8	10.0	30.5/28.9	3.15
Co	Original	110	0.05	1	0.51	**Sb**	Original	330	0.44	9.1	0.22
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	15	10	4.7		Addition	-	30	-	15
	Ass. value	1.10	14.0	10.1/10.7	5.04		Ass. value	33.0	25.5	9.2/7.82	13.2
Cr	Original	150	4.6	13	0.18	**Se**	Original	185	0.03	3.9	0.06
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	-	-	8		Addition	-	35	10	20
	Ass. value	15.0	4.64	13.4/13.1	7.82		Ass. value	18.5	35.1	13.9/15.3	19.8
Cu	Original	330	2.1	7.5	3	**Sn**	Original	175	0.02	0.006	0.03
	Dilution	10	-	-	-		Dilution	10	-	-	-
	Addition	-	20	10	-		Addition	-	10	35	2.5
	Ass. value	33.0	21.1	18.1/16.3	3.05		Ass. value	17.5	8.03	33.6/33.9	0.72
Fe	Original	2300	82	66	45	**Sr**	Original	200	1.6	150	81
	Dilution	10	-	-	-		Dilution	-	-	-	-
	Addition	-	-	100	-		Addition	-	14	-	-
	Ass. value	230	84.9	159/154	44.1		Ass. value	200	15.6	150/150	79.2

Measurand		A1M µg/l	P2M µg/l	TN3/ TY3 µg/l	V4M µg/l	Measurand		A1Hg µg/l	P2Hg µg/l	T3Hg µg/l	V4Hg µg/l
Ti	Original	355	1.4	0.8	0.4	**Hg**	Original	-	0.003	0.0007	0.0009
	Dilution	10	-	-	-		Dilution	-	-	-	-
	Addition	-	15	115	50		Addition	0.83	0.45	3.50	2.57
	Ass. value	35.5	16.0	116/125	50.1		Ass. value	0.84	0.44	3.47	2.29
V	Original	135	1.5	3.3	0.1						
	Dilution	10	-	-	-						
	Addition	-	5	130	-						
	Ass. value	13.5	6.19	132/138	35						
Zn	Original	545	22	170	45						
	Dilution	10	-	-	-						
	Addition	-	-	-	-						
	Ass. value	54.5	21.3	170/171	42.5						

Original = the original concentration
Dilution = the ratio of dilution
Addition = the addition concentration
Ass. value = the assigned value

APPENDIX 3: Homogeneity of the samples

Homogeneity was tested from duplicate measurements of three samples of selected measurands and each sample type.

Criteria for homogeneity:

$s_{anal}/s_h < 0.5$ and $s_{sam}^2 < c$, where

s_h = standard deviation for testing the homogeneity
s_{anal} = analytical deviation, standard deviation of the results in a sub sample
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_{anal}^2$, where
$s_{all}^2 = (0.3 \times s_{pt})^2$

F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

Measurand/Sample	Concentration [µg/l]	n	s_{pt} %	s_h%	s_h	s_{anal}	s_{anal}/s_h	s_{anal}/s_h<0.5?	s_{sam}^2	c	s_{sam}^2<c?
Cd/P2M	2.15	3	7.5	4.0	0.09	0.04	0.49	Yes	0.0003	0.01	Yes
Cr/P2M	4.52	3	7.5	2.8	0.13	0.06	0.49	Yes	0	0.02	Yes
Cu/P2M	20.5	3	10	1.5	0.31	0.06	0.18	Yes	0.04	0.04	Yes
Se/P2M	35.4	3	10	1.9	0.67	0.34	0.50	Yes	0	0.60	Yes
Ti/P2M	17.4	3	12.5	4.2	0.73	0.08	0.10	Yes	0.16	0.17	Yes
Zn/P2M	20.3	3	10	1.9	0.39	0.19	0.49	Yes	0.04	0.20	Yes
Cd/T3M	11.0	3	7.5	0.7	0.08	0.03	0.45	Yes	0.003	0.007	Yes
Cr/ T3M	13.8	3	10	3.0	0.41	0.20	0.49	Yes	0	0.22	Yes
Cu/ T3M	18.4	3	12.5	1.4	0.26	0.12	0.48	Yes	0.007	0.08	Yes
Se/ T3M	15.0	3	10	3.5	0.53	0.26	0.50	Yes	0	0.36	Yes
Ti/ T3M	117	3	5	2.4	2.82	1.40	0.50	Yes	0	10.5	Yes
Zn/ T3M	179	3	7.5	2.0	3.59	1.76	0.49	Yes	0	16.7	Yes
Cd/V4M	7.37	3	7.5	2.0	0.15	0.06	0.38	Yes	0.004	0.02	Yes
Cr/ V4M	7.97	3	7.5	2.4	0.19	0.10	0.50	Yes	0	0.05	Yes
Cu/ V4M	3.15	3	12.5	2.9	0.09	0.04	0.48	Yes	0.003	0.01	Yes
Se/ V4M	20.0	3	7.5	3.3	0.66	0.32	0.49	Yes	0	0.57	Yes
Ti/ V4M	50.2	3	5	2.2	1.11	0.05	0,05	Yes	0.33	0.34	Yes
Zn/ V4M	43.6	3	7.5	2.0	0.87	0.29	0.33	Yes	0.54	0.56	Yes
Hg/P2Hg*	0.43	3	10	9.1	0.04	0.002	0.06	Yes	0.0004	0.0004	Yes
Hg/T3Hg*	3.47	3	10	0.4	0.01	0.006	0.45	Yes	0.000002	0.0002	Yes
Hg/V4Hg*	2.24	3	-	9.3	0.21	0.10	0.50	Yes	0.02	0.06	Yes
Pb/P2M*	10.0	3	7.5	0.5	0.05	0.02	0.41	Yes	0.0005	0.002	Yes
Pb/T3M*	30.5	3	7.5	0.9	0.27	0.13	0.47	Yes	0	0.09	Yes
Pb/V4M*	3.15	3	10	0.8	0.03	0.01	0.50	Yes	0	0.0008	Yes

*) result based on the ID-ICP-MS measurement

s_{pt} % = standard deviation for proficiency assessment

Conclusion: All criteria for homogeneity were fulfilled and the samples could be considered homogenous.

APPENDIX 4: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical excecution	Action / Proftest SYKE
3	The participant received the samples on schedule. The samples were in reception of goods for five days.	The participant should check their within-laboratory delivery protocol. The samples were preserved with acids and a short storing time in the room temperature has not affected the sample stability and the results of measurands.
4	The participant received the samples one day after the estimated delivery day.	The samples were preserved with acids and short delay in the transport has no effect to the sample stability.
7	The participant didn't received the samples on schedule. The samples were stored at room temperature for five days before analysis.	According to the distributor's (Posti) tracking system the samples arrived at the participant on time. The participant should check their within-laboratory delivery protocol. The samples were preserved with acids and a short storing time in the room temperature has not affected the sample stability and the results of measurands.
All	The sample arrival form was not available from ProftestWEB after the sample delivery.	The provider corrected the mistake after the participant's note.

Participant	Comments to the results	Action / Proftest SYKE
6	The concentration ranges for Ba, Fe, Mn, Mo, Sb and Se in the sample V4M, were wrongly informed in the cover letter of the samples.	The provider apologies the mistake and will be more carefully with the information in the future.
11	The participant reported erroneously the result for Zn in the sample TY3.The corrected result was: 110 µg/l.	The result was outlier in the statistical treatment, and thus did not affect the performance evaluation. If the result had been reported correctly, the result would have been unsatisfactory based on evaluation with E_n score. The participant can re-calculate the E_n score according to the Guide for participants [4].
25	The participant reported erroneously the result for Zn in the sample TY3.The corrected result was: 183 µg/l.	The result was outlier in the statistical treatment, and thus did not affect the performance evaluation. The results were evaluated using E_n score. The participant did not report the expanded measurement uncertainty for the result, and thus no performance evaluation is given. The participant can re-calculate the E_n score according to the Guide for participants [4].

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
2, 5, 6, 7, 9, 10, 12, 13, 14, 15, 18, 22	The participants did not return the sample arrival document to the provider or delivered it late. The participants should follow the instructions of the provider.

APPENDIX 5: Evaluation of the assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
Al	A1M	µg/l	115	1	0.5	Calculated value	0.03
	P2M	µg/l	202	11	5.5	Median	0.28
	TN3	µg/l	79.2	4.4	5.6	Median	0.28
	TY3	µg/l	96.0	11.5	12	Median	0.48
	V4M	µg/l	110	6	5.8	Median	0.29
As	A1M	µg/l	55.0	0.3	0.6	Calculated value	0.06
	P2M	µg/l	11.2	0.7	6.2	Median	0.31
	TN3	µg/l	50.2	2.8	5.6	Robust mean	0.28
	TY3	µg/l	52.7	4.4	8.3	Median	
	V4M	µg/l	5.35	0.21	3.9	Median	0.20
B	A1M	µg/l	85.0	0.7	0.8	Calculated value	0.08
	P2M	µg/l	68.9	3.2	4.6	Median	0.23
	TN3	µg/l	157	13	8.0	Median	0.32
	TY3	µg/l	198	7	3.3	Median	
	V4M	µg/l	93.5	4.9	5.2	Mean	0.26
Ba	A1M	µg/l	130	1	0.6	Calculated value	0.06
	P2M	µg/l	198	10	4.8	Mean	0.32
	TN3	µg/l	74.2	4.1	5.5	Median	0.37
	TY3	µg/l	78.3	5.8	7.4	Median	
	V4M	µg/l	62.4	3.1	5.0	Median	0.33
Ca	A1M	mg/l	33.0	0.2	0.5	Calculated value	0.05
	P2M	mg/l	63.8	1.9	3.0	Median	0.30
	TN3	mg/l	65.5	1.2	1.9	Robust mean	0.19
	TY3	mg/l	65.6	3.5	5.4	Median	
	V4M	mg/l	33.9	0.6	1.9	Robust mean	0.19
Cd	A1M	µg/l	4.50	0.03	0.6	Calculated value	0.04
	P2M	µg/l	2.00	0.07	3.5	Median	0.23
	TN3	µg/l	9.96	0.39	3.9	Robust mean	0.26
	TY3	µg/l	10.7	0.7	6.7	Median	0.34
	V4M	µg/l	6.96	0.29	4.2	Robust mean	0.28
Co	A1M	µg/l	11.0	0.1	0.6	Calculated value	0.04
	P2M	µg/l	14.0	0.8	6.0	Median	0.30
	TN3	µg/l	10.1	0.7	7.2	Robust mean	0.36
	TY3	µg/l	10.7	0.8	7.6	Median	0.38
	V4M	µg/l	5.04	0.17	3.4	Mean	0.17
Cr	A1M	µg/l	15.0	0.1	0.8	Calculated value	0.05
	P2M	µg/l	4.64	0.24	5.2	Median	0.35
	TN3	µg/l	13.4	0.8	5.6	Robust mean	0.28
	TY3	µg/l	13.1	1.6	12	Median	0.48
	V4M	µg/l	7.82	0.46	5.9	Robust mean	0.39
Cu	A1M	µg/l	33.0	0.2	0.5	Calculated value	0.05
	P2M	µg/l	21.1	1.2	5.6	Robust mean	0.28
	TN3	µg/l	18.1	1.3	7.4	Robust mean	0.30
	TY3	µg/l	16.3	1.6	9.7	Median	0.39
	V4M	µg/l	3.05	0.3	9.0	Robust mean	0.36

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
Fe	A1M	µg/l	230	1	0.5	Calculated value	0.05
	P2M	µg/l	84.9	6.7	7.9	Median	0.32
	TN3	µg/l	159	6	3.9	Robust mean	0.26
	TY3	µg/l	154	9	6.0	Median	
	V4M	µg/l	44.1	1.9	4.2	Robust mean	0.28
Hg	A1Hg	µg/l	0.84	0.03	3.0	ID-ICP-MS	0.15
	P2Hg	µg/l	0.44	0.01	3.0	ID-ICP-MS	0.15
	T3Hg	µg/l	3.47	0.10	3.0	ID-ICP-MS	0.15
	V4Hg	µg/l	2.29	0.37	16	Median	
K	A1M	mg/l	25.0	0.1	0.4	Calculated value	0.04
	P2M	mg/l	36.1	0.8	2.1	Mean	0.21
	TN3	mg/l	43.8	0.7	1.5	Mean	0.15
	TY3	mg/l	43.1	1.9	4.3	Median	
	V4M	mg/l	21.8	0.5	2.3	Robust mean	0.23
Mg	A1M	mg/l	13.5	0.1	0.4	Calculated value	0.04
	P2M	mg/l	11.9	0.2	1.3	Median	0.13
	TN3	mg/l	19.7	0.5	2.6	Robust mean	0.26
	TY3	mg/l	19.3	1.0	5.3	Median	0.35
	V4M	mg/l	7.49	0.22	3.0	Robust mean	0.30
Mn	A1M	µg/l	45.9	0.3	0.6	Calculated value	0.06
	P2M	µg/l	18.0	1.3	7.3	Median	0.37
	TN3	µg/l	169	8	5.0	Robust mean	0.33
	TY3	µg/l	165	10	5.8	Median	
	V4M	µg/l	68.7	4.1	6.0	Robust mean	0.30
Mo	A1M	µg/l	22.5	0.2	0.8	Calculated value	0.08
	P2M	µg/l	6.20	0.41	6.6	Median	0.33
	TN3	µg/l	1202	34	2.8	Mean	0.28
	TY3	µg/l	1246	150	12	Mean	
	V4M	µg/l	12.3	0.8	6.7	Median	0.34
Ni	A1M	µg/l	17.5	0.1	0.7	Calculated value	0.07
	P2M	µg/l	10.5	0.5	5.1	Median	0.34
	TN3	µg/l	28.1	1.7	5.9	Robust mean	0.39
	TY3	µg/l	27.8	5.0	18	Median	
	V4M	µg/l	6.00	0.23	3.8	Median	0.25
Pb	A1M	µg/l	18.8	0.5	2.5	ID-ICP-MS	0.25
	P2M	µg/l	10.0	0	2.5	ID-ICP-MS	0.17
	TN3	µg/l	30.5	0.8	2.5	ID-ICP-MS	0.17
	TY3	µg/l	28.9	2.1	7.4	Median	0.37
	V4M	µg/l	3.15	0.08	2.5	ID-ICP-MS	0.13
Sb	A1M	µg/l	33.0	0.3	0.8	Calculated value	0.08
	P2M	µg/l	25.5	1.1	4.2	Median	0.28
	TN3	µg/l	9.2	0.8	8.9	Robust mean	0.45
	TY3	µg/l	7.82	0.50	6.4	Median	
	V4M	µg/l	13.2	0.9	6.6	Median	0.33
Se	A1M	µg/l	18.5	0.1	0.7	Calculated value	0.07
	P2M	µg/l	35.1	2.0	5.6	Mean	0.28
	TN3	µg/l	13.9	0.8	5.4	Mean	0.27
	TY3	µg/l	15.3	2.4	16	Median	
	V4M	µg/l	19.8	1.0	5.3	Median	0.35

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
Sn	A1M	µg/l	17.5	0.1	0.8	Calculated value	0.08
	P2M	µg/l	8.03	0.67	8.3	Mean	0.33
	TN3	µg/l	33.6	1.4	4.3	Mean	0.29
	TY3	µg/l	33.9	1.7	4.9	Median	
	V4M	µg/l	0.72	0.14	19	Median	
Sr	A1M	µg/l	110	1	0.6	Calculated value	0.06
	P2M	µg/l	200	11	5.6	Median	0.37
	TN3	µg/l	150	6	4.0	Median	0.27
	TY3	µg/l	150	0	0.2	Median	
	V4M	µg/l	79.2	2.4	3.0	Median	0.30
Ti	A1M	µg/l	35.5	0.2	0.7	Calculated value	0.07
	P2M	µg/l	16.0	1.5	9.3	Median	0.37
	TN3	µg/l	116	3	2.3	Median	0.23
	TY3	µg/l	125	6	4.6	Median	
	V4M	µg/l	50.1	1.2	2.3	Median	0.23
V	A1M	µg/l	13.5	0.1	0.7	Calculated value	0.07
	P2M	µg/l	6.19	0.33	5.4	Median	0.27
	TN3	µg/l	132	3	2.2	Median	0.15
	TY3	µg/l	138	15	11	Median	
	V4M	µg/l	34.6	1.3	3.8	Median	0.25
Zn	A1M	µg/l	54.5	0.3	0.6	Calculated value	0.06
	P2M	µg/l	21.3	1.9	9.1	Robust mean	0.46
	TN3	µg/l	170	7	4.3	Robust mean	0.29
	TY3	µg/l	171	22	13	Median	
	V4M	µg/l	42.5	1.3	3.0	Robust mean	0.20

U_{pt} = Expanded uncertainty of the assigned value
Criterion for reliability of the assigned value $u_{pt}/s_{pt} \leq 0.3$, where
s_{pt}= the standard deviation for proficiency assessment
u_{pt}= the standard uncertainty of the assigned value

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable, and the z scores are qualified.

APPENDIX 6: Terms in the results tables

Results of each participant

Measurand	The tested parameter
Sample	The code of the sample
z score	Calculated as follows: $z = (x_i - x_{pt})/s_{pt}$, where x_i = the result of the individual participant x_{pt} = the assigned value s_{pt} = the standard deviation for proficiency assessment
Assigned value	The value attributed to a particular property of a proficiency test item
2 × s_{pt} %	The standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level
Participant's result	The result reported by the participant (the mean value of the replicates)
Md	Median
s	Standard deviation
s %	Standard deviation, %
n_{stat}	Number of results in statistical processing

Summary on the z scores

S – satisfactory ($-2 \le z \le 2$)
Q – questionable ($2 < z < 3$), positive error, the result deviates more than 2 × s_{pt} from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than 2 × s_{pt} from the assigned value
U – unsatisfactory ($z \ge 3$), positive error, the result deviates more than 3 × s_{pt} from the assigned value
u – unsatisfactory ($z \le -3$), negative error, the result deviates more than 3 × s_{pt} from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as:
x^* = median of x_i ($i = 1, 2, \ldots, p$)
s^* = 1.483 × median of $|x_i - x^*|$ ($i = 1, 2, \ldots, p$)

The mean x^* and s^* are updated as follows:
Calculate $\varphi = 1.5 \times s^*$. A new value is then calculated for each result x_i ($i = 1, 2, \ldots, p$):

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi \\ x_i & \text{otherwise} \end{cases}$$

The new values of x^* and s^* are calculated from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences [2].

APPENDIX 7: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		2.09	115	15	133	112	112	12	10.9	13
	µg/l	P2M		2.48	202	20	252	202	199	16	8.2	9
	µg/l	TN3		1.73	79.2	20	92.9	79.2	79.3	7.3	9.3	11
	µg/l	TY3		0.42	96.0	25	101.0	96.0	94.4	14.4	15.3	7
	µg/l	V4M		1.45	110	20	126	110	110	10	9.1	10
As	µg/l	A1M		1.45	55.0	10	59.0	53.2	53.0	2.7	5.2	13
	µg/l	P2M		0.89	11.2	20	12.2	11.2	11.1	1.0	9.4	9
	µg/l	TN3		1.27	50.2	20	56.6	48.9	50.3	3.9	7.8	13
	µg/l	TY3			52.7		59.0	52.7	52.1	4.8	9.3	5
	µg/l	V4M		0.39	5.35	20	5.56	5.35	5.34	0.33	6.2	10
B	µg/l	A1M		2.07	85.0	10	93.8	81.2	80.4	6.5	8.1	10
	µg/l	P2M		2.63	68.9	20	87.0	68.9	67.2	4.1	6.1	7
	µg/l	TN3		1.22	157	25	181	157	158	19	12.0	9
	µg/l	TY3			198		186	198	196	6	3.3	4
	µg/l	V4M		1.44	93.5	20	107.0	92.9	93.5	7.3	7.8	9
Ba	µg/l	A1M		0.62	130	10	134	121	122	7	5.5	11
	µg/l	P2M		1.41	198	15	219	200	198	14	7.1	9
	µg/l	TN3		2.01	74.2	15	85.4	74.2	75.1	6.5	8.7	10
	µg/l	TY3			78.3		85.7	78.3	78.5	5.8	7.4	4
	µg/l	V4M		1.50	62.4	15	69.4	62.4	62.5	4.9	7.9	10
Ca	mg/l	A1M		0.42	33.0	10	33.7	32.8	32.7	0.9	2.7	14
	mg/l	P2M		1.03	63.8	10	67.1	63.8	63.8	3.1	4.9	11
	mg/l	TN3		0.92	65.5	10	68.5	65.8	65.4	1.9	2.9	15
	mg/l	TY3			65.6		70.2	65.6	66.7	3.1	4.6	3
	mg/l	V4M		-0.06	33.9	10	33.8	34.0	34.0	1.1	3.2	12
Cd	µg/l	A1M		0.33	4.50	15	4.61	4.47	4.43	0.23	5.2	13
	µg/l	P2M		0.80	2.00	15	2.12	2.00	2.00	0.12	5.8	11
	µg/l	TN3		0.72	9.96	15	10.50	10.00	9.96	0.53	5.3	13
	µg/l	TY3		0.19	10.7	20	10.9	10.7	10.8	0.9	8.2	6
	µg/l	V4M		0.67	6.96	15	7.31	7.08	6.93	0.42	6.1	12
Co	µg/l	A1M		1.21	11.0	15	12.0	10.5	10.4	0.8	7.6	16
	µg/l	P2M		2.07	14.0	20	16.9	14.0	14.2	1.4	9.9	11
	µg/l	TN3		2.18	10.1	20	12.3	10.0	10.1	1.1	11.1	13
	µg/l	TY3		1.78	10.7	20	12.6	10.7	11.0	1.0	9.3	6
	µg/l	V4M		1.19	5.04	20	5.64	4.97	5.04	0.27	5.3	10
Cr	µg/l	A1M		1.07	15.0	15	16.2	14.5	14.7	1.4	9.5	18
	µg/l	P2M		2.73	4.64	15	5.59	4.64	4.73	0.41	8.7	11
	µg/l	TN3		1.42	13.4	20	15.3	13.5	13.5	1.0	7.6	14
	µg/l	TY3		2.99	13.1	25	18.0	13.1	13.9	2.3	16.4	7
	µg/l	V4M		1.24	7.82	15	8.55	7.73	7.82	0.56	7.2	12
Cu	µg/l	A1M		1.27	33.0	10	35.1	31.6	31.6	1.7	5.4	18
	µg/l	P2M		1.99	21.1	20	25.3	21.0	21.2	1.8	8.5	13
	µg/l	TN3		0.80	18.1	25	19.9	17.5	18.1	1.9	10.6	15
	µg/l	TY3		2.06	16.3	25	20.5	16.3	16.8	2.0	11.9	6
	µg/l	V4M		0.94	3.05	25	3.4	3.0	3.1	0.4	12.7	13

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Fe	µg/l	A1M		1.65	230	10	249	223	223	13	5.8	21
	µg/l	P2M		1.42	84.9	25	100.0	84.9	83.9	11.0	13.1	11
	µg/l	TN3		2.18	159	15	185	159	159	11	6.7	18
	µg/l	TY3			154		176	154	158	11	6.7	5
	µg/l	V4M		2.06	44.1	15	50.9	43.8	44.3	2.8	6.4	12
Hg	µg/l	A1Hg		1.12	0.84	20	0.93	0.83	0.85	0.11	13.1	13
	µg/l	P2Hg		3.11	0.44	20	0.58	0.44	0.46	0.06	12.8	11
	µg/l	T3Hg		1.69	3.47	20	4.06	3.39	3.43	0.34	10.0	14
	µg/l	V4Hg			2.29		2.95	2.29	2.10	0.52	24.8	9
K	mg/l	A1M		-1.36	25.0	10	23.3	24.3	24.3	0.6	2.5	12
	mg/l	P2M		4.27	36.1	10	43.8	36.0	36.1	1.2	3.4	10
	mg/l	TN3		2.37	43.8	10	49.0	43.6	43.8	1.0	2.4	10
	mg/l	TY3			43.1		46.1	43.1	43.5	1.9	4.3	4
	mg/l	V4M		-0.37	21.8	10	21.4	22.0	21.8	0.6	2.9	12
Mg	mg/l	A1M		0.00	13.5	10	13.5	13.2	13.2	0.4	3.3	17
	mg/l	P2M		2.02	11.9	10	13.1	11.9	11.8	0.2	2.0	10
	mg/l	TN3		1.12	19.7	10	20.8	19.6	19.6	0.8	3.9	14
	mg/l	TY3		2.07	19.3	15	22.3	19.3	19.9	1.3	6.4	6
	mg/l	V4M		0.00	7.49	10	7.49	7.52	7.49	0.28	3.8	12
Mn	µg/l	A1M		1.70	45.9	10	49.8	44.4	44.6	3.2	7.2	17
	µg/l	P2M		1.83	18.0	20	21.3	18.0	18.4	2.2	12.1	11
	µg/l	TN3		1.74	169	15	191	172	169	12	7.2	16
	µg/l	TY3			165		183	165	169	10	5.8	4
	µg/l	V4M		0.80	68.7	20	74.2	68.2	68.7	5.0	7.3	12
Mo	µg/l	A1M		19.47	22.5	10	44.4	22.4	22.4	1.2	5.3	14
	µg/l	P2M		19.52	6.20	20	18.30	6.20	6.18	0.65	10.4	10
	µg/l	TN3		-17.10	1202	10	174	1181	1202	55	4.6	11
	µg/l	TY3			1246		183	1246	1246	107	8.6	2
	µg/l	V4M		46.34	12.3	20	69.3	12.3	12.6	1.3	10.1	9
Ni	µg/l	A1M		1.14	17.5	10	18.5	17.0	16.9	1.1	6.4	15
	µg/l	P2M		2.16	10.5	15	12.2	10.5	10.8	0.9	8.4	11
	µg/l	TN3		1.23	28.1	15	30.7	28.0	28.1	2.3	8.1	15
	µg/l	TY3			27.8		36.8	27.8	29.3	5.2	17.7	4
	µg/l	V4M		1.24	6.00	15	6.56	6.00	6.01	0.38	6.4	11
Pb	µg/l	A1M		-0.74	18.8	10	18.1	17.6	17.3	1.7	9.9	13
	µg/l	P2M		-0.24	10.0	15	10	9	9	1	15.0	11
	µg/l	TN3		0.22	30.5	15	31.0	27.4	27.8	3.6	12.8	11
	µg/l	TY3		0.42	28.9	20	30.1	28.9	28.6	2.6	9.1	6
	µg/l	V4M		0.06	3.15	20	3.17	2.79	2.78	0.39	14.0	11
Sb	µg/l	A1M		-2.24	33.0	10	29.3	31.7	31.7	2.0	6.4	12
	µg/l	P2M		-1.41	25.5	15	22.8	25.5	25.6	1.8	7.0	11
	µg/l	TN3		-1.33	9.2	20	8.0	8.9	9.2	1.0	11.1	12
	µg/l	TY3			7.82		7.74	7.82	7.96	0.51	6.4	4
	µg/l	V4M		-1.21	13.2	20	11.6	13.2	12.8	1.4	11.0	11

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Se	µg/l	A1M		2.81	18.5	10	21.1	18.5	18.6	1.5	8.1	12
	µg/l	P2M		1.85	35.1	20	41.6	35.6	35.1	3.3	9.3	11
	µg/l	TN3		1.58	13.9	20	16.1	13.6	13.9	1.2	9.0	11
	µg/l	TY3			15.3		17.0	15.3	14.8	2.4	16.5	4
	µg/l	V4M		1.55	19.8	15	22.1	19.8	19.4	1.7	8.9	11
Sn	µg/l	A1M		-1.83	17.5	10	15.9	16.9	16.8	1.0	5.9	11
	µg/l	P2M		-0.55	8.03	25	7.48	8.00	8.03	0.99	12.4	9
	µg/l	TN3		-0.08	33.6	15	33.4	32.8	33.6	2.3	6.8	10
	µg/l	TY3			33.9		34.5	33.9	33.6	1.7	4.9	4
	µg/l	V4M			0.72		0.63	0.72	0.76	0.19	24.7	7
Sr	µg/l	A1M		-16.73	110	10	18	106	106	5	5.1	9
	µg/l	P2M		1.80	200	15	227	200	199	16	7.9	8
	µg/l	TN3		1.51	150	15	167	150	148	9	6.3	10
	µg/l	TY3			150		175	150	150	0	0.1	3
	µg/l	V4M		1.62	79.2	10	85.6	79.2	80.7	3.7	4.5	9
Ti	µg/l	A1M		0.11	35.5	10	35.7	35.4	35.2	1.6	4.7	10
	µg/l	P2M		0.75	16.0	25	17.5	16.0	16.2	2.1	13.2	8
	µg/l	TN3		0.52	116	10	119	116	116	4	3.7	10
	µg/l	TY3			125		126	125	123	5	4.0	3
	µg/l	V4M		0.20	50.1	10	50.6	50.1	49.9	1.8	3.7	10
V	µg/l	A1M		2.22	13.5	10	15.0	13.1	13.3	0.8	5.9	10
	µg/l	P2M		2.21	6.19	20	7.56	6.19	6.35	0.54	8.6	10
	µg/l	TN3		2.02	132	15	152	132	132	4	3.3	9
	µg/l	TY3			138		157	138	142	14	9.8	3
	µg/l	V4M		1.43	34.6	15	38.3	34.6	34.3	2.0	5.9	10
Zn	µg/l	A1M		2.09	54.5	10	60.2	53.9	54.7	4.9	9.0	20
	µg/l	P2M		1.41	21.3	20	24.3	20.4	21.4	2.7	12.8	13
	µg/l	TN3		1.80	170	15	193	173	169	13	7.8	18
	µg/l	TY3			171		203	171	167	24	14.6	5
	µg/l	V4M		1.41	42.5	15	47.0	42.4	42.6	2.0	4.6	14

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cd	µg/l	TN3		0.19	9.96	15	10.10	10.00	9.96	0.53	5.3	13
Co	µg/l	TN3		17.82	10.1	20	28.1	10.0	10.1	1.1	11.1	13
Cr	µg/l	TN3		-1.04	13.4	20	12.0	13.5	13.5	1.0	7.6	14
Cu	µg/l	A1M		-0.97	33.0	10	31.4	31.6	31.6	1.7	5.4	18
Fe	µg/l	A1M		-0.04	230	10	230	223	223	13	5.8	21
	µg/l	TN3		0.45	159	15	164	159	159	11	6.7	18
Mg	mg/l	A1M		-0.44	13.5	10	13.2	13.2	13.2	0.4	3.3	17
	mg/l	TN3		0.00	19.7	10	19.7	19.6	19.6	0.8	3.9	14
Mn	µg/l	A1M		0.26	45.9	10	46.5	44.4	44.6	3.2	7.2	17
	µg/l	TN3		0.21	169	15	172	172	169	12	7.2	16
Mo	µg/l	A1M		-0.71	22.5	10	21.7	22.4	22.4	1.2	5.3	14
	µg/l	TN3		-0.27	1202	10	1186	1181	1202	55	4.6	11
Zn	µg/l	A1M		4.11	54.5	10	65.7	53.9	54.7	4.9	9.0	20
	µg/l	TN3		0.87	170	15	181	173	169	13	7.8	18

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ca	mg/l	A1M		0.61	33.0	10	34.0	32.8	32.7	0.9	2.7	14
	mg/l	TN3		0.43	65.5	10	66.9	65.8	65.4	1.9	2.9	15
Cu	µg/l	A1M		-0.18	33.0	10	32.7	31.6	31.6	1.7	5.4	18
	µg/l	TN3		1.50	18.1	25	21.5	17.5	18.1	1.9	10.6	15
Fe	µg/l	A1M		-2.09	230	10	206	223	223	13	5.8	21
	µg/l	TN3		-0.84	159	15	149	159	159	11	6.7	18
Mn	µg/l	A1M		-1.39	45.9	10	42.7	44.4	44.6	3.2	7.2	17
	µg/l	TN3		0.63	169	15	177	172	169	12	7.2	16
Zn	µg/l	A1M		0.48	54.5	10	55.8	53.9	54.7	4.9	9.0	20
	µg/l	TN3		1.02	170	15	183	173	169	13	7.8	18

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		1.97	115	15	132	112	112	12	10.9	13
	µg/l	TY3		1.75	96.0	25	117.0	96.0	94.4	14.4	15.3	7
Cr	µg/l	A1M		-1.16	15.0	15	13.7	14.5	14.7	1.4	9.5	18
	µg/l	TY3		-0.43	13.1	25	12.4	13.1	13.9	2.3	16.4	7
Cu	µg/l	A1M		-0.48	33.0	10	32.2	31.6	31.6	1.7	5.4	18
	µg/l	TY3		0.49	16.3	25	17.3	16.3	16.8	2.0	11.9	6
Fe	µg/l	A1M		0.61	230	10	237	223	223	13	5.8	21
	µg/l	TY3			154		159	154	158	11	6.7	5
Hg	µg/l	A1Hg		-0.52	0.84	20	0.80	0.83	0.85	0.11	13.1	13
	µg/l	T3Hg		-0.63	3.47	20	3.25	3.39	3.43	0.34	10.0	14
Mn	µg/l	A1M		-0.09	45.9	10	45.7	44.4	44.6	3.2	7.2	17
	µg/l	TY3			165		167	165	169	10	5.8	4
Ni	µg/l	A1M		0.34	17.5	10	17.8	17.0	16.9	1.1	6.4	15
	µg/l	TY3			27.8		28.1	27.8	29.3	5.2	17.7	4
Pb	µg/l	A1M		0.21	18.8	10	19.0	17.6	17.3	1.7	9.9	13
	µg/l	TY3		-0.52	28.9	20	27.4	28.9	28.6	2.6	9.1	6
Zn	µg/l	A1M		2.46	54.5	10	61.2	53.9	54.7	4.9	9.0	20
	µg/l	TY3			171		171	171	167	24	14.6	5

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-2.40	115	15	94	112	112	12	10.9	13
	µg/l	P2M		-1.34	202	20	175	202	199	16	8.2	9
	µg/l	TN3		-1.16	79.2	20	70.0	79.2	79.3	7.3	9.3	11
	µg/l	V4M		-1.97	110	20	88	110	110	10	9.1	10
As	µg/l	A1M		-1.05	55.0	10	52.1	53.2	53.0	2.7	5.2	13
	µg/l	P2M		-3.04	11.2	20	7.8	11.2	11.1	1.0	9.4	9
	µg/l	TN3		-0.42	50.2	20	48.1	48.9	50.3	3.9	7.8	13
	µg/l	V4M		-3.83	5.35	20	3.30	5.35	5.34	0.33	6.2	10
B	µg/l	A1M		-2.35	85.0	10	75.0	81.2	80.4	6.5	8.1	10
	µg/l	P2M		-2.32	68.9	20	52.9	68.9	67.2	4.1	6.1	7
	µg/l	TN3		-1.27	157	25	132	157	158	19	12.0	9
	µg/l	V4M		-1.97	93.5	20	75.1	92.9	93.5	7.3	7.8	9

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ba	µg/l	A1M		-1.54	130	10	120	121	122	7	5.5	11
	µg/l	P2M		-2.15	198	15	166	200	198	14	7.1	9
	µg/l	TN3		-1.53	74.2	15	65.7	74.2	75.1	6.5	8.7	10
	µg/l	V4M		-0.64	62.4	15	59.4	62.4	62.5	4.9	7.9	10
Ca	mg/l	A1M		-0.06	33.0	10	32.9	32.8	32.7	0.9	2.7	14
	mg/l	P2M		-1.76	63.8	10	58.2	63.8	63.8	3.1	4.9	11
	mg/l	TN3		-1.28	65.5	10	61.3	65.8	65.4	1.9	2.9	15
	mg/l	V4M		-0.29	33.9	10	33.4	34.0	34.0	1.1	3.2	12
Cd	µg/l	A1M		1.19	4.50	15	4.90	4.47	4.43	0.23	5.2	13
	µg/l	P2M		0.00	2.00	15	2.00	2.00	2.00	0.12	5.8	11
	µg/l	TN3		0.19	9.96	15	10.10	10.00	9.96	0.53	5.3	13
	µg/l	V4M		0.46	6.96	15	7.20	7.08	6.93	0.42	6.1	12
Co	µg/l	A1M		-0.36	11.0	15	10.7	10.5	10.4	0.8	7.6	16
	µg/l	P2M		-0.71	14.0	20	13.0	14.0	14.2	1.4	9.9	11
	µg/l	TN3		-0.20	10.1	20	9.9	10.0	10.1	1.1	11.1	13
	µg/l	V4M		-0.08	5.04	20	5.00	4.97	5.04	0.27	5.3	10
Cr	µg/l	A1M		0.62	15.0	15	15.7	14.5	14.7	1.4	9.5	18
	µg/l	P2M		0.75	4.64	15	4.90	4.64	4.73	0.41	8.7	11
	µg/l	TN3		0.30	13.4	20	13.8	13.5	13.5	1.0	7.6	14
	µg/l	V4M		1.50	7.82	15	8.70	7.73	7.82	0.56	7.2	12
Cu	µg/l	A1M		-0.42	33.0	10	32.3	31.6	31.6	1.7	5.4	18
	µg/l	P2M		0.52	21.1	20	22.2	21.0	21.2	1.8	8.5	13
	µg/l	TN3		0.00	18.1	25	18.1	17.5	18.1	1.9	10.6	15
	µg/l	V4M		1.44	3.05	25	3.6	3.0	3.1	0.4	12.7	13
Fe	µg/l	A1M		-1.04	230	10	218	223	223	13	5.8	21
	µg/l	P2M		-1.25	84.9	25	71.6	84.9	83.9	11.0	13.1	11
	µg/l	TN3		-1.17	159	15	145	159	159	11	6.7	18
	µg/l	V4M		-0.39	44.1	15	42.8	43.8	44.3	2.8	6.4	12
Hg	µg/l	A1Hg		-0.42	0.84	20	0.81	0.83	0.85	0.11	13.1	13
	µg/l	P2Hg		-1.16	0.44	20	0.39	0.44	0.46	0.06	12.8	11
	µg/l	T3Hg		-0.50	3.47	20	3.30	3.39	3.43	0.34	10.0	14
	µg/l	V4Hg			2.29		1.22	2.29	2.10	0.52	24.8	9
K	mg/l	A1M		-0.08	25.0	10	24.9	24.3	24.3	0.6	2.5	12
	mg/l	P2M		0.55	36.1	10	37.1	36.0	36.1	1.2	3.4	10
	mg/l	TN3		0.05	43.8	10	43.9	43.6	43.8	1.0	2.4	10
	mg/l	V4M		0.55	21.8	10	22.4	22.0	21.8	0.6	2.9	12
Mg	mg/l	A1M		-0.15	13.5	10	13.4	13.2	13.2	0.4	3.3	17
	mg/l	P2M		0.00	11.9	10	11.9	11.9	11.8	0.2	2.0	10
	mg/l	TN3		-0.41	19.7	10	19.3	19.6	19.6	0.8	3.9	14
	mg/l	V4M		0.13	7.49	10	7.54	7.52	7.49	0.28	3.8	12
Mn	µg/l	A1M		-1.74	45.9	10	41.9	44.4	44.6	3.2	7.2	17
	µg/l	P2M		-1.28	18.0	20	15.7	18.0	18.4	2.2	12.1	11
	µg/l	TN3		-1.66	169	15	148	172	169	12	7.2	16
	µg/l	V4M		-0.64	68.7	20	64.3	68.2	68.7	5.0	7.3	12
Mo	µg/l	A1M		0.36	22.5	10	22.9	22.4	22.4	1.2	5.3	14
	µg/l	P2M		-2.90	6.20	20	4.40	6.20	6.18	0.65	10.4	10
	µg/l	TN3		-0.70	1202	10	1160	1181	1202	55	4.6	11
	µg/l	V4M		1.79	12.3	20	14.5	12.3	12.6	1.3	10.1	9

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ni	µg/l	A1M		1.03	17.5	10	18.4	17.0	16.9	1.1	6.4	15
	µg/l	P2M		1.02	10.5	15	11.3	10.5	10.8	0.9	8.4	11
	µg/l	TN3		0.05	28.1	15	28.2	28.0	28.1	2.3	8.1	15
	µg/l	V4M		0.22	6.00	15	6.10	6.00	6.01	0.38	6.4	11
Pb	µg/l	A1M		0.53	18.8	10	19.3	17.6	17.3	1.7	9.9	13
	µg/l	P2M		1.20	10.0	15	11	9	9	1	15.0	11
	µg/l	TN3		1.75	30.5	15	34.5	27.4	27.8	3.6	12.8	11
	µg/l	V4M		14.76	3.15	20	7.80	2.79	2.78	0.39	14.0	11
Sb	µg/l	A1M		-0.91	33.0	10	31.5	31.7	31.7	2.0	6.4	12
	µg/l	P2M		-0.52	25.5	15	24.5	25.5	25.6	1.8	7.0	11
	µg/l	TN3		-1.20	9.2	20	8.1	8.9	9.2	1.0	11.1	12
	µg/l	V4M		0.23	13.2	20	13.5	13.2	12.8	1.4	11.0	11
Se	µg/l	A1M		0.00	18.5	10	18.5	18.5	18.6	1.5	8.1	12
	µg/l	P2M		-0.60	35.1	20	33.0	35.6	35.1	3.3	9.3	11
	µg/l	TN3		0.86	13.9	20	15.1	13.6	13.9	1.2	9.0	11
	µg/l	V4M		0.00	19.8	15	19.8	19.8	19.4	1.7	8.9	11
Sn	µg/l	A1M		-1.60	17.5	10	16.1	16.9	16.8	1.0	5.9	11
	µg/l	P2M		-1.23	8.03	25	6.80	8.00	8.03	0.99	12.4	9
	µg/l	TN3		-0.83	33.6	15	31.5	32.8	33.6	2.3	6.8	10
	µg/l	V4M			0.72		0.10	0.72	0.76	0.19	24.7	7
Sr	µg/l	A1M		-0.73	110	10	106	106	106	5	5.1	9
	µg/l	P2M		-1.53	200	15	177	200	199	16	7.9	8
	µg/l	TN3		-1.42	150	15	134	150	148	9	6.3	10
	µg/l	V4M		-0.45	79.2	10	77.4	79.2	80.7	3.7	4.5	9
Ti	µg/l	A1M		1.01	35.5	10	37.3	35.4	35.2	1.6	4.7	10
	µg/l	P2M		0.70	16.0	25	17.4	16.0	16.2	2.1	13.2	8
	µg/l	TN3		-1.03	116	10	110	116	116	4	3.7	10
	µg/l	V4M		0.64	50.1	10	51.7	50.1	49.9	1.8	3.7	10
V	µg/l	A1M		0.00	13.5	10	13.5	13.1	13.3	0.8	5.9	10
	µg/l	P2M		-0.31	6.19	20	6.00	6.19	6.35	0.54	8.6	10
	µg/l	TN3		-0.71	132	15	125	132	132	4	3.3	9
	µg/l	V4M		0.00	34.6	15	34.6	34.6	34.3	2.0	5.9	10
Zn	µg/l	A1M		-1.47	54.5	10	50.5	53.9	54.7	4.9	9.0	20
	µg/l	P2M		-1.64	21.3	20	17.8	20.4	21.4	2.7	12.8	13
	µg/l	TN3		-1.41	170	15	152	173	169	13	7.8	18
	µg/l	V4M		-0.97	42.5	15	39.4	42.4	42.6	2.0	4.6	14

Participant 6												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Al	µg/l	A1M		-0.49	115	15	111	112	112	12	10.9	13
	µg/l	P2M		0.11	202	20	204	202	199	16	8.2	9
	µg/l	TN3		0.01	79.2	20	79.3	79.2	79.3	7.3	9.3	11
	µg/l	TY3		-0.09	96.0	25	94.9	96.0	94.4	14.4	15.3	7
	µg/l	V4M		0.04	110	20	110	110	110	10	9.1	10
As	µg/l	A1M		-0.65	55.0	10	53.2	53.2	53.0	2.7	5.2	13
	µg/l	P2M		-0.27	11.2	20	10.9	11.2	11.1	1.0	9.4	9
	µg/l	TN3		-0.60	50.2	20	47.2	48.9	50.3	3.9	7.8	13
	µg/l	TY3			52.7		46.2	52.7	52.1	4.8	9.3	5
	µg/l	V4M		-0.11	5.35	20	5.29	5.35	5.34	0.33	6.2	10
B	µg/l	A1M			85.0	10	*< 200*	81.2	80.4	6.5	8.1	10
	µg/l	P2M			68.9	20	*< 200*	68.9	67.2	4.1	6.1	7
	µg/l	TN3		2.85	157	25	213	157	158	19	12.0	9
	µg/l	TY3			198		200	198	196	6	3.3	4
	µg/l	V4M			93.5	20	*< 200*	92.9	93.5	7.3	7.8	9
Ba	µg/l	A1M		-0.80	130	10	125	121	122	7	5.5	11
	µg/l	P2M		0.17	198	15	201	200	198	14	7.1	9
	µg/l	TN3		0.83	74.2	15	78.8	74.2	75.1	6.5	8.7	10
	µg/l	TY3			78.3		79.2	78.3	78.5	5.8	7.4	4
	µg/l	V4M		0.41	62.4	15	64.3	62.4	62.5	4.9	7.9	10
Ca	mg/l	A1M		-0.42	33.0	10	32.3	32.8	32.7	0.9	2.7	14
	mg/l	P2M		1.76	63.8	10	69.4	63.8	63.8	3.1	4.9	11
	mg/l	TN3		-0.06	65.5	10	65.3	65.8	65.4	1.9	2.9	15
	mg/l	TY3			65.6		65.6	65.6	66.7	3.1	4.6	3
	mg/l	V4M		1.47	33.9	10	36.4	34.0	34.0	1.1	3.2	12
Cd	µg/l	A1M		0.44	4.50	15	4.65	4.47	4.43	0.23	5.2	13
	µg/l	P2M		0.20	2.00	15	2.03	2.00	2.00	0.12	5.8	11
	µg/l	TN3		0.32	9.96	15	10.20	10.00	9.96	0.53	5.3	13
	µg/l	TY3		-0.47	10.7	20	10.2	10.7	10.8	0.9	8.2	6
	µg/l	V4M		-0.31	6.96	15	6.80	7.08	6.93	0.42	6.1	12
Co	µg/l	A1M		-0.85	11.0	15	10.3	10.5	10.4	0.8	7.6	16
	µg/l	P2M		-0.36	14.0	20	13.5	14.0	14.2	1.4	9.9	11
	µg/l	TN3		0.40	10.1	20	10.5	10.0	10.1	1.1	11.1	13
	µg/l	TY3		-0.37	10.7	20	10.3	10.7	11.0	1.0	9.3	6
	µg/l	V4M		-0.42	5.04	20	4.83	4.97	5.04	0.27	5.3	10
Cr	µg/l	A1M		-0.71	15.0	15	14.2	14.5	14.7	1.4	9.5	18
	µg/l	P2M		0.40	4.64	15	4.78	4.64	4.73	0.41	8.7	11
	µg/l	TN3		-0.22	13.4	20	13.1	13.5	13.5	1.0	7.6	14
	µg/l	TY3		0.00	13.1	25	13.1	13.1	13.9	2.3	16.4	7
	µg/l	V4M		-0.31	7.82	15	7.64	7.73	7.82	0.56	7.2	12
Cu	µg/l	A1M		-1.52	33.0	10	30.5	31.6	31.6	1.7	5.4	18
	µg/l	P2M		-0.81	21.1	20	19.4	21.0	21.2	1.8	8.5	13
	µg/l	TN3		-0.88	18.1	25	16.1	17.5	18.1	1.9	10.6	15
	µg/l	TY3		0.05	16.3	25	16.4	16.3	16.8	2.0	11.9	6
	µg/l	V4M		-0.76	3.05	25	2.8	3.0	3.1	0.4	12.7	13

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Fe	µg/l	A1M		-0.63	230	10	223	223	223	13	5.8	21
	µg/l	P2M		-1.02	84.9	25	74.1	84.9	83.9	11.0	13.1	11
	µg/l	TN3		-0.29	159	15	156	159	159	11	6.7	18
	µg/l	TY3			154		154	154	158	11	6.7	5
	µg/l	V4M		-0.91	44.1	15	41.1	43.8	44.3	2.8	6.4	12
Hg	µg/l	A1Hg		1.43	0.84	20	0.96	0.83	0.85	0.11	13.1	13
	µg/l	P2Hg		2.05	0.44	20	0.53	0.44	0.46	0.06	12.8	11
	µg/l	T3Hg		0.00	3.47	20	3.47	3.39	3.43	0.34	10.0	14
	µg/l	V4Hg			2.29		2.33	2.29	2.10	0.52	24.8	9
K	mg/l	A1M		-0.96	25.0	10	23.8	24.3	24.3	0.6	2.5	12
	mg/l	P2M		-0.72	36.1	10	34.8	36.0	36.1	1.2	3.4	10
	mg/l	TN3		-0.27	43.8	10	43.2	43.6	43.8	1.0	2.4	10
	mg/l	TY3			43.1		41.7	43.1	43.5	1.9	4.3	4
	mg/l	V4M		1.01	21.8	10	22.9	22.0	21.8	0.6	2.9	12
Mg	mg/l	A1M		-0.44	13.5	10	13.2	13.2	13.2	0.4	3.3	17
	mg/l	P2M		-0.17	11.9	10	11.8	11.9	11.8	0.2	2.0	10
	mg/l	TN3		0.20	19.7	10	19.9	19.6	19.6	0.8	3.9	14
	mg/l	TY3		-0.14	19.3	15	19.1	19.3	19.9	1.3	6.4	6
	mg/l	V4M		1.36	7.49	10	8.00	7.52	7.49	0.28	3.8	12
Mn	µg/l	A1M		-1.44	45.9	10	42.6	44.4	44.6	3.2	7.2	17
	µg/l	P2M		-0.33	18.0	20	17.4	18.0	18.4	2.2	12.1	11
	µg/l	TN3		-0.66	169	15	161	172	169	12	7.2	16
	µg/l	TY3			165		162	165	169	10	5.8	4
	µg/l	V4M		-0.28	68.7	20	66.8	68.2	68.7	5.0	7.3	12
Mo	µg/l	A1M		0.09	22.5	10	22.6	22.4	22.4	1.2	5.3	14
	µg/l	P2M		0.32	6.20	20	6.40	6.20	6.18	0.65	10.4	10
	µg/l	TN3		2.35	1202	10	1343	1181	1202	55	4.6	11
	µg/l	TY3			1246		1321	1246	1246	107	8.6	2
	µg/l	V4M		-0.81	12.3	20	11.3	12.3	12.6	1.3	10.1	9
Ni	µg/l	A1M		-1.49	17.5	10	16.2	17.0	16.9	1.1	6.4	15
	µg/l	P2M		-0.51	10.5	15	10.1	10.5	10.8	0.9	8.4	11
	µg/l	TN3		-1.28	28.1	15	25.4	28.0	28.1	2.3	8.1	15
	µg/l	TY3			27.8		24.9	27.8	29.3	5.2	17.7	4
	µg/l	V4M		-0.20	6.00	15	5.91	6.00	6.01	0.38	6.4	11
Pb	µg/l	A1M		-1.60	18.8	10	17.3	17.6	17.3	1.7	9.9	13
	µg/l	P2M		-1.60	10.0	15	9	9	9	1	15.0	11
	µg/l	TN3		-1.36	30.5	15	27.4	27.4	27.8	3.6	12.8	11
	µg/l	TY3		-0.28	28.9	20	28.1	28.9	28.6	2.6	9.1	6
	µg/l	V4M		-0.86	3.15	20	2.88	2.79	2.78	0.39	14.0	11
Sb	µg/l	A1M		-1.09	33.0	10	31.2	31.7	31.7	2.0	6.4	12
	µg/l	P2M		0.47	25.5	15	26.4	25.5	25.6	1.8	7.0	11
	µg/l	TN3		-0.65	9.2	20	8.6	8.9	9.2	1.0	11.1	12
	µg/l	TY3			7.82		7.50	7.82	7.96	0.51	6.4	4
	µg/l	V4M		0.23	13.2	20	13.5	13.2	12.8	1.4	11.0	11

Participant 6												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Se	µg/l	A1M		0.86	18.5	10	19.3	18.5	18.6	1.5	8.1	12
	µg/l	P2M		0.14	35.1	20	35.6	35.6	35.1	3.3	9.3	11
	µg/l	TN3		-0.43	13.9	20	13.3	13.6	13.9	1.2	9.0	11
	µg/l	TY3			15.3		11.7	15.3	14.8	2.4	16.5	4
	µg/l	V4M		0.34	19.8	15	20.3	19.8	19.4	1.7	8.9	11
Sn	µg/l	A1M		-0.69	17.5	10	16.9	16.9	16.8	1.0	5.9	11
	µg/l	P2M		0.77	8.03	25	8.80	8.00	8.03	0.99	12.4	9
	µg/l	TN3		-0.60	33.6	15	32.1	32.8	33.6	2.3	6.8	10
	µg/l	TY3			33.9		31.5	33.9	33.6	1.7	4.9	4
Sn	µg/l	V4M			0.72		*< 10*	0.72	0.76	0.19	24.7	7
Sr	µg/l	A1M		-0.80	110	10	106	106	106	5	5.1	9
	µg/l	P2M		0.04	200	15	201	200	199	16	7.9	8
	µg/l	TN3		0.04	150	15	150	150	148	9	6.3	10
	µg/l	TY3			150		150	150	150	0	0.1	3
	µg/l	V4M		-0.03	79.2	10	79.1	79.2	80.7	3.7	4.5	9
Ti	µg/l	A1M		0.96	35.5	10	37.2	35.4	35.2	1.6	4.7	10
	µg/l	P2M		2.65	16.0	25	21.3	16.0	16.2	2.1	13.2	8
	µg/l	TN3		0.98	116	10	122	116	116	4	3.7	10
	µg/l	TY3			125		125	125	123	5	4.0	3
	µg/l	V4M		0.92	50.1	10	52.4	50.1	49.9	1.8	3.7	10
V	µg/l	A1M		-1.19	13.5	10	12.7	13.1	13.3	0.8	5.9	10
	µg/l	P2M		-0.10	6.19	20	6.13	6.19	6.35	0.54	8.6	10
	µg/l	TN3		0.31	132	15	135	132	132	4	3.3	9
	µg/l	TY3			138		130	138	142	14	9.8	3
	µg/l	V4M		-0.58	34.6	15	33.1	34.6	34.3	2.0	5.9	10
Zn	µg/l	A1M		-0.29	54.5	10	53.7	53.9	54.7	4.9	9.0	20
	µg/l	P2M		-1.03	21.3	20	19.1	20.4	21.4	2.7	12.8	13
	µg/l	TN3		-2.60	170	15	137	173	169	13	7.8	18
	µg/l	TY3			171		138	171	167	24	14.6	5
	µg/l	V4M		-0.41	42.5	15	41.2	42.4	42.6	2.0	4.6	14

Participant 7												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Al	µg/l	A1M		-3.07	115	15	89	112	112	12	10.9	13
	µg/l	P2M		-1.09	202	20	180	202	199	16	8.2	9
	µg/l	TN3		-1.48	79.2	20	67.5	79.2	79.3	7.3	9.3	11
	µg/l	V4M		-2.32	110	20	85	110	110	10	9.1	10
As	µg/l	A1M		-2.00	55.0	10	49.5	53.2	53.0	2.7	5.2	13
	µg/l	P2M		-1.07	11.2	20	10.0	11.2	11.1	1.0	9.4	9
	µg/l	TN3		-0.44	50.2	20	48.0	48.9	50.3	3.9	7.8	13
	µg/l	V4M		-0.65	5.35	20	5.00	5.35	5.34	0.33	6.2	10
B	µg/l	A1M		0.00	85.0	10	85.0	81.2	80.4	6.5	8.1	10
	µg/l	P2M		-0.06	68.9	20	68.5	68.9	67.2	4.1	6.1	7
	µg/l	TN3		-0.61	157	25	145	157	158	19	12.0	9
	µg/l	V4M		0.27	93.5	20	96.0	92.9	93.5	7.3	7.8	9

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ba	µg/l	A1M		-3.08	130	10	110	121	122	7	5.5	11
	µg/l	P2M		-1.21	198	15	180	200	198	14	7.1	9
	µg/l	TN3		-1.20	74.2	15	67.5	74.2	75.1	6.5	8.7	10
	µg/l	V4M		-1.69	62.4	15	54.5	62.4	62.5	4.9	7.9	10
Ca	mg/l	A1M		2.42	33.0	10	37.0	32.8	32.7	0.9	2.7	14
	mg/l	P2M		0.38	63.8	10	65.0	63.8	63.8	3.1	4.9	11
	mg/l	TN3		0.31	65.5	10	66.5	65.8	65.4	1.9	2.9	15
	mg/l	V4M		-0.53	33.9	10	33.0	34.0	34.0	1.1	3.2	12
Cd	µg/l	A1M		-1.48	4.50	15	4.00	4.47	4.43	0.23	5.2	13
	µg/l	P2M		0.00	2.00	15	2.00	2.00	2.00	0.12	5.8	11
	µg/l	TN3		-1.29	9.96	15	9.00	10.00	9.96	0.53	5.3	13
	µg/l	V4M		-1.84	6.96	15	6.00	7.08	6.93	0.42	6.1	12
Co	µg/l	A1M		-1.82	11.0	15	9.5	10.5	10.4	0.8	7.6	16
	µg/l	P2M		-0.71	14.0	20	13.0	14.0	14.2	1.4	9.9	11
	µg/l	TN3		-1.09	10.1	20	9.0	10.0	10.1	1.1	11.1	13
	µg/l	V4M		-2.06	5.04	20	4.00	4.97	5.04	0.27	5.3	10
Cr	µg/l	A1M		-1.78	15.0	15	13.0	14.5	14.7	1.4	9.5	18
	µg/l	P2M		-0.40	4.64	15	4.50	4.64	4.73	0.41	8.7	11
	µg/l	TN3		-0.67	13.4	20	12.5	13.5	13.5	1.0	7.6	14
	µg/l	V4M		-1.40	7.82	15	7.00	7.73	7.82	0.56	7.2	12
Cu	µg/l	A1M		-1.21	33.0	10	31.0	31.6	31.6	1.7	5.4	18
	µg/l	P2M		-0.05	21.1	20	21.0	21.0	21.2	1.8	8.5	13
	µg/l	TN3		-0.27	18.1	25	17.5	17.5	18.1	1.9	10.6	15
	µg/l	V4M		-0.13	3.05	25	3.0	3.0	3.1	0.4	12.7	13
Fe	µg/l	A1M		-18.00	230	10	23	223	223	13	5.8	21
	µg/l	P2M		-7.25	84.9	25	8.0	84.9	83.9	11.0	13.1	11
	µg/l	TN3		0.92	159	15	170	159	159	11	6.7	18
	µg/l	V4M		-0.18	44.1	15	43.5	43.8	44.3	2.8	6.4	12
K	mg/l	A1M		-0.80	25.0	10	24.0	24.3	24.3	0.6	2.5	12
	mg/l	P2M		-0.33	36.1	10	35.5	36.0	36.1	1.2	3.4	10
	mg/l	TN3		-0.59	43.8	10	42.5	43.6	43.8	1.0	2.4	10
	mg/l	V4M		-0.73	21.8	10	21.0	22.0	21.8	0.6	2.9	12
Mg	mg/l	A1M		-0.74	13.5	10	13.0	13.2	13.2	0.4	3.3	17
	mg/l	P2M		0.17	11.9	10	12.0	11.9	11.8	0.2	2.0	10
	mg/l	TN3		0.81	19.7	10	20.5	19.6	19.6	0.8	3.9	14
	mg/l	V4M		-1.31	7.49	10	7.00	7.52	7.49	0.28	3.8	12
Mn	µg/l	A1M		-3.44	45.9	10	38.0	44.4	44.6	3.2	7.2	17
	µg/l	P2M		-1.94	18.0	20	14.5	18.0	18.4	2.2	12.1	11
	µg/l	TN3		-1.50	169	15	150	172	169	12	7.2	16
	µg/l	V4M		-1.19	68.7	20	60.5	68.2	68.7	5.0	7.3	12
Mo	µg/l	A1M		-1.33	22.5	10	21.0	22.4	22.4	1.2	5.3	14
	µg/l	P2M		-0.32	6.20	20	6.00	6.20	6.18	0.65	10.4	10
	µg/l	TN3		-0.03	1202	10	1200	1181	1202	55	4.6	11
	µg/l	V4M		-1.46	12.3	20	10.5	12.3	12.6	1.3	10.1	9
Ni	µg/l	A1M		-1.14	17.5	10	16.5	17.0	16.9	1.1	6.4	15
	µg/l	P2M		-0.63	10.5	15	10.0	10.5	10.8	0.9	8.4	11
	µg/l	TN3		-0.52	28.1	15	27.0	28.0	28.1	2.3	8.1	15
	µg/l	V4M		0.00	6.00	15	6.00	6.00	6.01	0.38	6.4	11

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Pb	µg/l	A1M		-5.64	18.8	10	13.5	17.6	17.3	1.7	9.9	13
	µg/l	P2M		-4.00	10.0	15	7	9	9	1	15.0	11
	µg/l	TN3		-4.15	30.5	15	21.0	27.4	27.8	3.6	12.8	11
	µg/l	V4M		-3.65	3.15	20	2.00	2.79	2.78	0.39	14.0	11
Sb	µg/l	A1M		-1.82	33.0	10	30.0	31.7	31.7	2.0	6.4	12
	µg/l	P2M		0.00	25.5	15	25.5	25.5	25.6	1.8	7.0	11
	µg/l	TN3		-0.76	9.2	20	8.5	8.9	9.2	1.0	11.1	12
	µg/l	V4M		-0.15	13.2	20	13.0	13.2	12.8	1.4	11.0	11
Se	µg/l	A1M		-3.78	18.5	10	15.0	18.5	18.6	1.5	8.1	12
	µg/l	P2M		-1.31	35.1	20	30.5	35.6	35.1	3.3	9.3	11
	µg/l	TN3		-1.01	13.9	20	12.5	13.6	13.9	1.2	9.0	11
	µg/l	V4M		-2.56	19.8	15	16.0	19.8	19.4	1.7	8.9	11
Sn	µg/l	A1M		-2.29	17.5	10	15.5	16.9	16.8	1.0	5.9	11
	µg/l	P2M		-0.03	8.03	25	8.00	8.00	8.03	0.99	12.4	9
	µg/l	TN3		-0.63	33.6	15	32.0	32.8	33.6	2.3	6.8	10
	µg/l	V4M			0.72		1.00	0.72	0.76	0.19	24.7	7
Sr	µg/l	A1M		-2.73	110	10	95	106	106	5	5.1	9
	µg/l	P2M		-1.33	200	15	180	200	199	16	7.9	8
	µg/l	TN3		-1.33	150	15	135	150	148	9	6.3	10
	µg/l	V4M		-1.94	79.2	10	71.5	79.2	80.7	3.7	4.5	9
Ti	µg/l	A1M		-1.69	35.5	10	32.5	35.4	35.2	1.6	4.7	10
	µg/l	P2M		-1.00	16.0	25	14.0	16.0	16.2	2.1	13.2	8
	µg/l	TN3		-1.03	116	10	110	116	116	4	3.7	10
	µg/l	V4M		-1.04	50.1	10	47.5	50.1	49.9	1.8	3.7	10
V	µg/l	A1M		0.74	13.5	10	14.0	13.1	13.3	0.8	5.9	10
	µg/l	P2M		1.31	6.19	20	7.00	6.19	6.35	0.54	8.6	10
	µg/l	TN3		0.81	132	15	140	132	132	4	3.3	9
	µg/l	V4M		0.35	34.6	15	35.5	34.6	34.3	2.0	5.9	10
Zn	µg/l	A1M		-1.10	54.5	10	51.5	53.9	54.7	4.9	9.0	20
	µg/l	P2M		-0.61	21.3	20	20.0	20.4	21.4	2.7	12.8	13
	µg/l	TN3		-12.04	170	15	17	173	169	13	7.8	18
	µg/l	V4M		-0.16	42.5	15	42.0	42.4	42.6	2.0	4.6	14

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
As	µg/l	TN3		0.36	50.2	20	52.0	48.9	50.3	3.9	7.8	13
Cd	µg/l	TY3		-0.65	10.7	20	10.0	10.7	10.8	0.9	8.2	6
Fe	µg/l	TN3		-3.52	159	15	117	159	159	11	6.7	18
Zn	µg/l	TN3		-0.63	170	15	162	173	169	13	7.8	18

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
As	µg/l	A1M		0.36	55.0	10	56.0	53.2	53.0	2.7	5.2	13
	µg/l	P2M		2.23	11.2	20	13.7	11.2	11.1	1.0	9.4	9
	µg/l	TN3		0.36	50.2	20	52.0	48.9	50.3	3.9	7.8	13
	µg/l	V4M		4.58	5.35	20	7.80	5.35	5.34	0.33	6.2	10
Cd	µg/l	A1M		0.00	4.50	15	4.50	4.47	4.43	0.23	5.2	13
	µg/l	P2M		-1.33	2.00	15	1.80	2.00	2.00	0.12	5.8	11
	µg/l	TN3		-0.62	9.96	15	9.50	10.00	9.96	0.53	5.3	13
	µg/l	V4M		0.08	6.96	15	7.00	7.08	6.93	0.42	6.1	12
Co	µg/l	A1M		0.00	11.0	15	11.0	10.5	10.4	0.8	7.6	16
	µg/l	P2M		-1.21	14.0	20	12.3	14.0	14.2	1.4	9.9	11
	µg/l	TN3		-0.50	10.1	20	9.6	10.0	10.1	1.1	11.1	13
	µg/l	V4M		-0.48	5.04	20	4.80	4.97	5.04	0.27	5.3	10
Cr	µg/l	A1M		-0.89	15.0	15	14.0	14.5	14.7	1.4	9.5	18
	µg/l	P2M		-1.26	4.64	15	4.20	4.64	4.73	0.41	8.7	11
	µg/l	TN3		-0.82	13.4	20	12.3	13.5	13.5	1.0	7.6	14
	µg/l	V4M		-0.72	7.82	15	7.40	7.73	7.82	0.56	7.2	12
Cu	µg/l	A1M		-1.21	33.0	10	31.0	31.6	31.6	1.7	5.4	18
	µg/l	P2M		-0.19	21.1	20	20.7	21.0	21.2	1.8	8.5	13
	µg/l	TN3		-0.93	18.1	25	16.0	17.5	18.1	1.9	10.6	15
	µg/l	V4M		-0.39	3.05	25	2.9	3.0	3.1	0.4	12.7	13
Fe	µg/l	A1M		-1.28	230	10	215	223	223	13	5.8	21
	µg/l	P2M		-1.56	84.9	25	68.3	84.9	83.9	11.0	13.1	11
	µg/l	TN3		-1.43	159	15	142	159	159	11	6.7	18
	µg/l	V4M		-0.94	44.1	15	41.0	43.8	44.3	2.8	6.4	12
Hg	µg/l	A1Hg		-1.07	0.84	20	0.75	0.83	0.85	0.11	13.1	13
	µg/l	P2Hg		0.00	0.44	20	0.44	0.44	0.46	0.06	12.8	11
	µg/l	T3Hg		-0.92	3.47	20	3.15	3.39	3.43	0.34	10.0	14
	µg/l	V4Hg			2.29		2.29	2.29	2.10	0.52	24.8	9
Mo	µg/l	A1M		-0.44	22.5	10	22.0	22.4	22.4	1.2	5.3	14
	µg/l	P2M		-0.81	6.20	20	5.70	6.20	6.18	0.65	10.4	10
	µg/l	TN3		-2.38	1202	10	1059	1181	1202	55	4.6	11
	µg/l	V4M		0.00	12.3	20	12.3	12.3	12.6	1.3	10.1	9
Ni	µg/l	A1M		-0.91	17.5	10	16.7	17.0	16.9	1.1	6.4	15
	µg/l	P2M		-0.89	10.5	15	9.8	10.5	10.8	0.9	8.4	11
	µg/l	TN3		-1.47	28.1	15	25.0	28.0	28.1	2.3	8.1	15
	µg/l	V4M		-0.67	6.00	15	5.70	6.00	6.01	0.38	6.4	11
Pb	µg/l	A1M		-1.60	18.8	10	17.3	17.6	17.3	1.7	9.9	13
	µg/l	P2M		-3.60	10.0	15	7	9	9	1	15.0	11
	µg/l	TN3		-2.84	30.5	15	24.0	27.4	27.8	3.6	12.8	11
	µg/l	V4M		-2.38	3.15	20	2.40	2.79	2.78	0.39	14.0	11
Sb	µg/l	A1M		0.79	33.0	10	34.3	31.7	31.7	2.0	6.4	12
	µg/l	P2M		-0.42	25.5	15	24.7	25.5	25.6	1.8	7.0	11
	µg/l	TN3		1.20	9.2	20	10.3	8.9	9.2	1.0	11.1	12
	µg/l	V4M		-2.58	13.2	20	9.8	13.2	12.8	1.4	11.0	11
Se	µg/l	A1M		1.95	18.5	10	20.3	18.5	18.6	1.5	8.1	12
	µg/l	P2M		0.54	35.1	20	37.0	35.6	35.1	3.3	9.3	11
	µg/l	TN3		-1.15	13.9	20	12.3	13.6	13.9	1.2	9.0	11
	µg/l	V4M		0.61	19.8	15	20.7	19.8	19.4	1.7	8.9	11

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Zn	µg/l	A1M		0.29	54.5	10	55.3	53.9	54.7	4.9	9.0	20
	µg/l	P2M		-0.94	21.3	20	19.3	20.4	21.4	2.7	12.8	13
	µg/l	TN3		-0.47	170	15	164	173	169	13	7.8	18
	µg/l	V4M		-0.06	42.5	15	42.3	42.4	42.6	2.0	4.6	14

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
As	µg/l	TY3			52.7		49.2	52.7	52.1	4.8	9.3	5
	µg/l	V4M		0.97	5.35	20	5.87	5.35	5.34	0.33	6.2	10
Cd	µg/l	TY3		-0.19	10.7	20	10.5	10.7	10.8	0.9	8.2	6
Cu	µg/l	P2M		-1.28	21.1	20	18.4	21.0	21.2	1.8	8.5	13
	µg/l	TY3		-0.74	16.3	25	14.8	16.3	16.8	2.0	11.9	6
	µg/l	V4M			3.05	25	*<10*	3.0	3.1	0.4	12.7	13
Fe	µg/l	A1M		-2.70	230	10	199	223	223	13	5.8	21
	µg/l	P2M		2.27	84.9	25	109.0	84.9	83.9	11.0	13.1	11
Hg	µg/l	A1Hg		9275.71	0.84	20	780.00	0.83	0.85	0.11	13.1	13
	µg/l	P2Hg		9194.55	0.44	20	405.00	0.44	0.46	0.06	12.8	11
	µg/l	T3Hg		-0.84	3.47	20	3.18	3.39	3.43	0.34	10.0	14
	µg/l	V4Hg			2.29		1.40	2.29	2.10	0.52	24.8	9
Ni	µg/l	V4M			6.00	15	*<5*	6.00	6.01	0.38	6.4	11
Pb	µg/l	TY3		1.04	28.9	20	31.9	28.9	28.6	2.6	9.1	6
	µg/l	V4M		-1.40	3.15	20	2.71	2.79	2.78	0.39	14.0	11
Zn	µg/l	P2M		1.69	21.3	20	24.9	20.4	21.4	2.7	12.8	13
	µg/l	TY3			171		171	171	167	24	14.6	5
	µg/l	V4M		0.47	42.5	15	44.0	42.4	42.6	2.0	4.6	14

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		4.06	115	15	150	112	112	12	10.9	13
	µg/l	TY3		0.00	96.0	25	96.0	96.0	94.4	14.4	15.3	7
Co	µg/l	A1M		0.00	11.0	15	11.0	10.5	10.4	0.8	7.6	16
	µg/l	TY3		1.21	10.7	20	12.0	10.7	11.0	1.0	9.3	6
Cr	µg/l	A1M		0.89	15.0	15	16.0	14.5	14.7	1.4	9.5	18
	µg/l	TY3		1.77	13.1	25	16.0	13.1	13.9	2.3	16.4	7
Fe	µg/l	A1M		-2.43	230	10	202	223	223	13	5.8	21
	µg/l	TY3			154		150	154	158	11	6.7	5
Mg	mg/l	A1M		-0.81	13.5	10	13.0	13.2	13.2	0.4	3.3	17
	mg/l	TY3		-0.03	19.3	15	19.3	19.3	19.9	1.3	6.4	6
Zn	µg/l	A1M		-14.13	54.5	10	16.0	53.9	54.7	4.9	9.0	20
	µg/l	TY3			171		11	171	167	24	14.6	5

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-0.34	115	15	112	112	112	12	10.9	13
	µg/l	P2M		-0.02	202	20	202	202	199	16	8.2	9
	µg/l	TY3		-1.82	96.0	25	74.2	96.0	94.4	14.4	15.3	7
	µg/l	V4M		-0.45	110	20	105	110	110	10	9.1	10
As	µg/l	A1M		-0.56	55.0	10	53.5	53.2	53.0	2.7	5.2	13
	µg/l	P2M		0.68	11.2	20	12.0	11.2	11.1	1.0	9.4	9
	µg/l	TY3			52.7		53.6	52.7	52.1	4.8	9.3	5
	µg/l	V4M		0.09	5.35	20	5.40	5.35	5.34	0.33	6.2	10
B	µg/l	A1M		-2.18	85.0	10	75.8	81.2	80.4	6.5	8.1	10
	µg/l	P2M		0.01	68.9	20	69.0	68.9	67.2	4.1	6.1	7
	µg/l	TY3			198		197	198	196	6	3.3	4
	µg/l	V4M		-0.30	93.5	20	90.7	92.9	93.5	7.3	7.8	9
Ba	µg/l	A1M		-2.60	130	10	113	121	122	7	5.5	11
	µg/l	P2M		0.11	198	15	200	200	198	14	7.1	9
	µg/l	TY3			78.3		71.5	78.3	78.5	5.8	7.4	4
	µg/l	V4M		0.50	62.4	15	64.7	62.4	62.5	4.9	7.9	10
Ca	mg/l	A1M		-0.11	33.0	10	32.8	32.8	32.7	0.9	2.7	14
	mg/l	P2M		0.39	63.8	10	65.0	63.8	63.8	3.1	4.9	11
	mg/l	TN3		0.08	65.5	10	65.8	65.8	65.4	1.9	2.9	15
	mg/l	V4M		0.21	33.9	10	34.3	34.0	34.0	1.1	3.2	12
Cd	µg/l	A1M		-0.24	4.50	15	4.42	4.47	4.43	0.23	5.2	13
	µg/l	P2M		0.93	2.00	15	2.14	2.00	2.00	0.12	5.8	11
	µg/l	TY3		1.67	10.7	20	12.5	10.7	10.8	0.9	8.2	6
	µg/l	V4M		0.37	6.96	15	7.15	7.08	6.93	0.42	6.1	12
Co	µg/l	A1M		-1.51	11.0	15	9.8	10.5	10.4	0.8	7.6	16
	µg/l	P2M		0.35	14.0	20	14.5	14.0	14.2	1.4	9.9	11
	µg/l	TY3		-0.19	10.7	20	10.5	10.7	11.0	1.0	9.3	6
	µg/l	V4M		-0.27	5.04	20	4.90	4.97	5.04	0.27	5.3	10
Cr	µg/l	A1M		-1.86	15.0	15	12.9	14.5	14.7	1.4	9.5	18
	µg/l	P2M		-0.42	4.64	15	4.49	4.64	4.73	0.41	8.7	11
	µg/l	TY3		-0.69	13.1	25	12.0	13.1	13.9	2.3	16.4	7
	µg/l	V4M		-1.25	7.82	15	7.09	7.73	7.82	0.56	7.2	12
Cu	µg/l	A1M		-3.25	33.0	10	27.6	31.6	31.6	1.7	5.4	18
	µg/l	P2M		-0.45	21.1	20	20.2	21.0	21.2	1.8	8.5	13
	µg/l	TY3		-0.03	16.3	25	16.2	16.3	16.8	2.0	11.9	6
	µg/l	V4M		-0.71	3.05	25	2.8	3.0	3.1	0.4	12.7	13
Fe	µg/l	A1M		-1.72	230	10	210	223	223	13	5.8	21
	µg/l	P2M		0.00	84.9	25	84.9	84.9	83.9	11.0	13.1	11
	µg/l	TN3		-0.51	159	15	153	159	159	11	6.7	18
	µg/l	V4M		-0.71	44.1	15	41.8	43.8	44.3	2.8	6.4	12
Hg	µg/l	A1Hg		-2.23	0.84	20	0.65	0.83	0.85	0.11	13.1	13
	µg/l	P2Hg		-0.82	0.44	20	0.40	0.44	0.46	0.06	12.8	11
	µg/l	T3Hg		-2.26	3.47	20	2.69	3.39	3.43	0.34	10.0	14
	µg/l	V4Hg			2.29		1.23	2.29	2.10	0.52	24.8	9
K	mg/l	A1M		-0.38	25.0	10	24.5	24.3	24.3	0.6	2.5	12
	mg/l	P2M		-0.68	36.1	10	34.9	36.0	36.1	1.2	3.4	10
	mg/l	TY3			43.1		43.0	43.1	43.5	1.9	4.3	4
	mg/l	V4M		-0.70	21.8	10	21.0	22.0	21.8	0.6	2.9	12

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Mg	mg/l	A1M		0.82	13.5	10	14.1	13.2	13.2	0.4	3.3	17
	mg/l	P2M		0.38	11.9	10	12.1	11.9	11.8	0.2	2.0	10
	mg/l	TY3		0.82	19.3	15	20.5	19.3	19.9	1.3	6.4	6
	mg/l	V4M		0.59	7.49	10	7.71	7.52	7.49	0.28	3.8	12
Mn	µg/l	A1M		-1.70	45.9	10	42.0	44.4	44.6	3.2	7.2	17
	µg/l	P2M		-0.43	18.0	20	17.2	18.0	18.4	2.2	12.1	11
	µg/l	TN3		0.39	169	15	174	172	169	12	7.2	16
	µg/l	V4M		-0.86	68.7	20	62.8	68.2	68.7	5.0	7.3	12
Mo	µg/l	A1M		-2.55	22.5	10	19.6	22.4	22.4	1.2	5.3	14
	µg/l	P2M		-1.58	6.20	20	5.22	6.20	6.18	0.65	10.4	10
	µg/l	TN3		-0.35	1202	10	1181	1181	1202	55	4.6	11
	µg/l	V4M		-2.68	12.3	20	9.0	12.3	12.6	1.3	10.1	9
Ni	µg/l	A1M		-3.18	17.5	10	14.7	17.0	16.9	1.1	6.4	15
	µg/l	P2M		0.01	10.5	15	10.5	10.5	10.8	0.9	8.4	11
	µg/l	TN3		-0.87	28.1	15	26.3	28.0	28.1	2.3	8.1	15
	µg/l	V4M		-1.11	6.00	15	5.50	6.00	6.01	0.38	6.4	11
Pb	µg/l	A1M		-3.59	18.8	10	15.4	17.6	17.3	1.7	9.9	13
	µg/l	P2M		-2.27	10.0	15	8	9	9	1	15.0	11
	µg/l	TY3		-1.56	28.9	20	24.4	28.9	28.6	2.6	9.1	6
	µg/l	V4M		-1.70	3.15	20	2.61	2.79	2.78	0.39	14.0	11
Sb	µg/l	A1M		-3.12	33.0	10	27.9	31.7	31.7	2.0	6.4	12
	µg/l	P2M		-0.83	25.5	15	23.9	25.5	25.6	1.8	7.0	11
	µg/l	TY3			7.82		7.90	7.82	7.96	0.51	6.4	4
	µg/l	V4M		-1.56	13.2	20	11.1	13.2	12.8	1.4	11.0	11
Se	µg/l	A1M		0.71	18.5	10	19.2	18.5	18.6	1.5	8.1	12
	µg/l	P2M		0.63	35.1	20	37.3	35.6	35.1	3.3	9.3	11
	µg/l	TY3			15.3		16.5	15.3	14.8	2.4	16.5	4
	µg/l	V4M		-1.54	19.8	15	17.5	19.8	19.4	1.7	8.9	11
Sn	µg/l	A1M		1.64	17.5	10	18.9	16.9	16.8	1.0	5.9	11
	µg/l	P2M		3.65	8.03	25	11.69	8.00	8.03	0.99	12.4	9
	µg/l	TY3			33.9		33.3	33.9	33.6	1.7	4.9	4
	µg/l	V4M			0.72		0.88	0.72	0.76	0.19	24.7	7
Sr	µg/l	A1M		-0.11	110	10	109	106	106	5	5.1	9
	µg/l	P2M		-0.29	200	15	196	200	199	16	7.9	8
	µg/l	TY3			150		150	150	150	0	0.1	3
	µg/l	V4M		-0.23	79.2	10	78.3	79.2	80.7	3.7	4.5	9
Ti	µg/l	A1M		0.63	35.5	10	36.6	35.4	35.2	1.6	4.7	10
	µg/l	P2M		1.92	16.0	25	19.8	16.0	16.2	2.1	13.2	8
	µg/l	TN3		0.68	116	10	120	116	116	4	3.7	10
	µg/l	V4M		0.59	50.1	10	51.6	50.1	49.9	1.8	3.7	10
V	µg/l	A1M		-1.87	13.5	10	12.2	13.1	13.3	0.8	5.9	10
	µg/l	P2M		-0.47	6.19	20	5.90	6.19	6.35	0.54	8.6	10
	µg/l	TN3		-0.06	132	15	131	132	132	4	3.3	9
	µg/l	V4M		-1.58	34.6	15	30.5	34.6	34.3	2.0	5.9	10
Zn	µg/l	A1M		-0.73	54.5	10	52.5	53.9	54.7	4.9	9.0	20
	µg/l	P2M		2.77	21.3	20	27.2	20.4	21.4	2.7	12.8	13
	µg/l	TN3		0.39	170	15	175	173	169	13	7.8	18
	µg/l	V4M		-0.31	42.5	15	41.5	42.4	42.6	2.0	4.6	14

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-0.23	115	15	113	112	112	12	10.9	13
	µg/l	TN3		87.35	79.2	20	771.0	79.2	79.3	7.3	9.3	11
As	µg/l	A1M		-1.49	55.0	10	50.9	53.2	53.0	2.7	5.2	13
	µg/l	TN3		-0.32	50.2	20	48.6	48.9	50.3	3.9	7.8	13
Ba	µg/l	A1M		-1.38	130	10	121	121	122	7	5.5	11
	µg/l	TN3		-0.66	74.2	15	70.5	74.2	75.1	6.5	8.7	10
Ca	mg/l	A1M		-0.78	33.0	10	31.7	32.8	32.7	0.9	2.7	14
	mg/l	TN3		-0.45	65.5	10	64.0	65.8	65.4	1.9	2.9	15
Cd	µg/l	A1M		0.00	4.50	15	4.50	4.47	4.43	0.23	5.2	13
	µg/l	TN3		0.05	9.96	15	10.00	10.00	9.96	0.53	5.3	13
Co	µg/l	A1M		-0.61	11.0	15	10.5	10.5	10.4	0.8	7.6	16
	µg/l	TN3		-0.35	10.1	20	9.8	10.0	10.1	1.1	11.1	13
Cr	µg/l	A1M		0.44	15.0	15	15.5	14.5	14.7	1.4	9.5	18
	µg/l	TN3		0.75	13.4	20	14.4	13.5	13.5	1.0	7.6	14
Cu	µg/l	A1M		-0.61	33.0	10	32.0	31.6	31.6	1.7	5.4	18
	µg/l	TN3		1.50	18.1	25	21.5	17.5	18.1	1.9	10.6	15
Fe	µg/l	A1M		-0.70	230	10	222	223	223	13	5.8	21
	µg/l	TN3		0.08	159	15	160	159	159	11	6.7	18
Hg	µg/l	A1Hg		-0.67	0.84	20	0.78	0.83	0.85	0.11	13.1	13
	µg/l	T3Hg		-0.28	3.47	20	3.37	3.39	3.43	0.34	10.0	14
Mg	mg/l	A1M		-1.72	13.5	10	12.3	13.2	13.2	0.4	3.3	17
	mg/l	TN3		-1.77	19.7	10	18.0	19.6	19.6	0.8	3.9	14
Mn	µg/l	A1M		-1.09	45.9	10	43.4	44.4	44.6	3.2	7.2	17
	µg/l	TN3		-0.47	169	15	163	172	169	12	7.2	16
Mo	µg/l	A1M		-0.49	22.5	10	22.0	22.4	22.4	1.2	5.3	14
	µg/l	TN3		-0.62	1202	10	1165	1181	1202	55	4.6	11
Ni	µg/l	A1M		0.11	17.5	10	17.6	17.0	16.9	1.1	6.4	15
	µg/l	TN3		1.90	28.1	15	32.1	28.0	28.1	2.3	8.1	15
Pb	µg/l	A1M		-3.19	18.8	10	15.8	17.6	17.3	1.7	9.9	13
	µg/l	TN3		-1.40	30.5	15	27.3	27.4	27.8	3.6	12.8	11
Sb	µg/l	A1M		0.73	33.0	10	34.2	31.7	31.7	2.0	6.4	12
	µg/l	TN3		1.41	9.2	20	10.5	8.9	9.2	1.0	11.1	12
Se	µg/l	A1M		-0.32	18.5	10	18.2	18.5	18.6	1.5	8.1	12
	µg/l	TN3		-0.22	13.9	20	13.6	13.6	13.9	1.2	9.0	11
Sn	µg/l	A1M		-1.94	17.5	10	15.8	16.9	16.8	1.0	5.9	11
	µg/l	TN3		-0.95	33.6	15	31.2	32.8	33.6	2.3	6.8	10
Sr	µg/l	A1M		34.73	110	10	301	106	106	5	5.1	9
	µg/l	TN3		-0.53	150	15	144	150	148	9	6.3	10
Zn	µg/l	A1M		-0.18	54.5	10	54.0	53.9	54.7	4.9	9.0	20
	µg/l	TN3		0.39	170	15	175	173	169	13	7.8	18

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		5.80	115	15	165	112	112	12	10.9	13
	µg/l	TN3		14.62	79.2	20	195.0	79.2	79.3	7.3	9.3	11
As	µg/l	TN3		3.17	50.2	20	66.1	48.9	50.3	3.9	7.8	13
Ca	mg/l	A1M		-0.55	33.0	10	32.1	32.8	32.7	0.9	2.7	14
	mg/l	TN3		0.43	65.5	10	66.9	65.8	65.4	1.9	2.9	15
Co	µg/l	A1M		-0.36	11.0	15	10.7	10.5	10.4	0.8	7.6	16
	µg/l	TN3		0.50	10.1	20	10.6	10.0	10.1	1.1	11.1	13
Cr	µg/l	A1M		2.67	15.0	15	18.0	14.5	14.7	1.4	9.5	18
	µg/l	TN3		3.43	13.4	20	18.0	13.5	13.5	1.0	7.6	14
Cu	µg/l	A1M		-0.36	33.0	10	32.4	31.6	31.6	1.7	5.4	18
	µg/l	TN3		-0.75	18.1	25	16.4	17.5	18.1	1.9	10.6	15
Fe	µg/l	A1M		-0.70	230	10	222	223	223	13	5.8	21
	µg/l	TN3		0.42	159	15	164	159	159	11	6.7	18
Mg	mg/l	A1M		-0.74	13.5	10	13.0	13.2	13.2	0.4	3.3	17
	mg/l	TN3		0.20	19.7	10	19.9	19.6	19.6	0.8	3.9	14
Mn	µg/l	A1M		0.48	45.9	10	47.0	44.4	44.6	3.2	7.2	17
	µg/l	TN3		1.42	169	15	187	172	169	12	7.2	16
Ni	µg/l	A1M		15.54	17.5	10	31.1	17.0	16.9	1.1	6.4	15
	µg/l	TN3		0.66	28.1	15	29.5	28.0	28.1	2.3	8.1	15
Sb	µg/l	TN3		-0.87	9.2	20	8.4	8.9	9.2	1.0	11.1	12
Zn	µg/l	A1M		-3.85	54.5	10	44.0	53.9	54.7	4.9	9.0	20
	µg/l	TN3		-0.31	170	15	166	173	169	13	7.8	18

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		0.23	115	15	117	112	112	12	10.9	13
	µg/l	P2M		-0.40	202	20	194	202	199	16	8.2	9
	µg/l	TN3		-0.38	79.2	20	76.2	79.2	79.3	7.3	9.3	11
	µg/l	TY3		-1.48	96.0	25	78.3	96.0	94.4	14.4	15.3	7
	µg/l	V4M		-0.09	110	20	109	110	110	10	9.1	10
As	µg/l	A1M		-1.38	55.0	10	51.2	53.2	53.0	2.7	5.2	13
	µg/l	P2M		-1.10	11.2	20	10.0	11.2	11.1	1.0	9.4	9
	µg/l	TN3		0.02	50.2	20	50.3	48.9	50.3	3.9	7.8	13
	µg/l	TY3			52.7		52.7	52.7	52.1	4.8	9.3	5
	µg/l	V4M		-0.73	5.35	20	4.96	5.35	5.34	0.33	6.2	10
B	µg/l	A1M		-1.04	85.0	10	80.6	81.2	80.4	6.5	8.1	10
	µg/l	P2M		0.00	68.9	20	68.9	68.9	67.2	4.1	6.1	7
	µg/l	TN3		1.53	157	25	187	157	158	19	12.0	9
	µg/l	TY3			198		199	198	196	6	3.3	4
	µg/l	V4M		-0.15	93.5	20	92.1	92.9	93.5	7.3	7.8	9
Ba	µg/l	A1M		-0.92	130	10	124	121	122	7	5.5	11
	µg/l	P2M		-0.34	198	15	193	200	198	14	7.1	9
	µg/l	TN3		0.22	74.2	15	75.4	74.2	75.1	6.5	8.7	10
	µg/l	TY3			78.3		77.4	78.3	78.5	5.8	7.4	4
	µg/l	V4M		-0.34	62.4	15	60.8	62.4	62.5	4.9	7.9	10

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ca	mg/l	A1M		-0.42	33.0	10	32.3	32.8	32.7	0.9	2.7	14
	mg/l	P2M		-0.16	63.8	10	63.3	63.8	63.8	3.1	4.9	11
	mg/l	TN3		-0.21	65.5	10	64.8	65.8	65.4	1.9	2.9	15
	mg/l	TY3			65.6		64.3	65.6	66.7	3.1	4.6	3
	mg/l	V4M		0.06	33.9	10	34.0	34.0	34.0	1.1	3.2	12
Cd	µg/l	A1M		-0.62	4.50	15	4.29	4.47	4.43	0.23	5.2	13
	µg/l	P2M		0.33	2.00	15	2.05	2.00	2.00	0.12	5.8	11
	µg/l	TN3		-1.06	9.96	15	9.17	10.00	9.96	0.53	5.3	13
	µg/l	TY3		0.19	10.7	20	10.9	10.7	10.8	0.9	8.2	6
	µg/l	V4M		-0.29	6.96	15	6.81	7.08	6.93	0.42	6.1	12
Co	µg/l	A1M		-0.85	11.0	15	10.3	10.5	10.4	0.8	7.6	16
	µg/l	P2M		0.43	14.0	20	14.6	14.0	14.2	1.4	9.9	11
	µg/l	TN3		0.69	10.1	20	10.8	10.0	10.1	1.1	11.1	13
	µg/l	TY3		0.19	10.7	20	10.9	10.7	11.0	1.0	9.3	6
	µg/l	V4M		-0.20	5.04	20	4.94	4.97	5.04	0.27	5.3	10
Cr	µg/l	A1M		-0.71	15.0	15	14.2	14.5	14.7	1.4	9.5	18
	µg/l	P2M		-1.01	4.64	15	4.29	4.64	4.73	0.41	8.7	11
	µg/l	TN3		0.00	13.4	20	13.4	13.5	13.5	1.0	7.6	14
	µg/l	TY3		0.61	13.1	25	14.1	13.1	13.9	2.3	16.4	7
	µg/l	V4M		-0.60	7.82	15	7.47	7.73	7.82	0.56	7.2	12
Cu	µg/l	A1M		-1.82	33.0	10	30.0	31.6	31.6	1.7	5.4	18
	µg/l	P2M		-0.33	21.1	20	20.4	21.0	21.2	1.8	8.5	13
	µg/l	TN3		-1.02	18.1	25	15.8	17.5	18.1	1.9	10.6	15
	µg/l	TY3		-0.34	16.3	25	15.6	16.3	16.8	2.0	11.9	6
	µg/l	V4M		-0.92	3.05	25	2.7	3.0	3.1	0.4	12.7	13
Fe	µg/l	A1M		-0.96	230	10	219	223	223	13	5.8	21
	µg/l	P2M		-0.98	84.9	25	74.5	84.9	83.9	11.0	13.1	11
	µg/l	TN3		-0.67	159	15	151	159	159	11	6.7	18
	µg/l	TY3			154		151	154	158	11	6.7	5
	µg/l	V4M		-0.36	44.1	15	42.9	43.8	44.3	2.8	6.4	12
Hg	µg/l	A1Hg		-0.13	0.84	20	0.83	0.83	0.85	0.11	13.1	13
	µg/l	P2Hg		1.20	0.44	20	0.49	0.44	0.46	0.06	12.8	11
	µg/l	T3Hg		-0.46	3.47	20	3.31	3.39	3.43	0.34	10.0	14
	µg/l	V4Hg			2.29		2.52	2.29	2.10	0.52	24.8	9
K	mg/l	A1M		-0.72	25.0	10	24.1	24.3	24.3	0.6	2.5	12
	mg/l	P2M		0.11	36.1	10	36.3	36.0	36.1	1.2	3.4	10
	mg/l	TN3		0.00	43.8	10	43.8	43.6	43.8	1.0	2.4	10
	mg/l	TY3			43.1		43.3	43.1	43.5	1.9	4.3	4
	mg/l	V4M		0.18	21.8	10	22.0	22.0	21.8	0.6	2.9	12
Mg	mg/l	A1M		-0.15	13.5	10	13.4	13.2	13.2	0.4	3.3	17
	mg/l	P2M		-0.50	11.9	10	11.6	11.9	11.8	0.2	2.0	10
	mg/l	TN3		-0.61	19.7	10	19.1	19.6	19.6	0.8	3.9	14
	mg/l	TY3		0.07	19.3	15	19.4	19.3	19.9	1.3	6.4	6
	mg/l	V4M		0.51	7.49	10	7.68	7.52	7.49	0.28	3.8	12

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Mn	µg/l	A1M		-1.05	45.9	10	43.5	44.4	44.6	3.2	7.2	17
	µg/l	P2M		-0.17	18.0	20	17.7	18.0	18.4	2.2	12.1	11
	µg/l	TN3		-0.71	169	15	160	172	169	12	7.2	16
	µg/l	TY3			165		163	165	169	10	5.8	4
	µg/l	V4M		-0.16	68.7	20	67.6	68.2	68.7	5.0	7.3	12
Mo	µg/l	A1M		-0.27	22.5	10	22.2	22.4	22.4	1.2	5.3	14
	µg/l	P2M		1.19	6.20	20	6.94	6.20	6.18	0.65	10.4	10
	µg/l	TN3		-0.53	1202	10	1170	1181	1202	55	4.6	11
	µg/l	TY3			1246		1170	1246	1246	107	8.6	2
	µg/l	V4M		-0.08	12.3	20	12.2	12.3	12.6	1.3	10.1	9
Ni	µg/l	A1M		-2.40	17.5	10	15.4	17.0	16.9	1.1	6.4	15
	µg/l	P2M		-0.69	10.5	15	10.0	10.5	10.8	0.9	8.4	11
	µg/l	TN3		-1.71	28.1	15	24.5	28.0	28.1	2.3	8.1	15
	µg/l	TY3			27.8		27.4	27.8	29.3	5.2	17.7	4
	µg/l	V4M		-1.36	6.00	15	5.39	6.00	6.01	0.38	6.4	11
Pb	µg/l	A1M		-1.28	18.8	10	17.6	17.6	17.3	1.7	9.9	13
	µg/l	P2M		-2.07	10.0	15	8	9	9	1	15.0	11
	µg/l	TN3		-1.31	30.5	15	27.5	27.4	27.8	3.6	12.8	11
	µg/l	TY3		0.24	28.9	20	29.6	28.9	28.6	2.6	9.1	6
	µg/l	V4M		-1.14	3.15	20	2.79	2.79	2.78	0.39	14.0	11
Sb	µg/l	A1M		-0.67	33.0	10	31.9	31.7	31.7	2.0	6.4	12
	µg/l	P2M		0.00	25.5	15	25.5	25.5	25.6	1.8	7.0	11
	µg/l	TN3		-0.87	9.2	20	8.4	8.9	9.2	1.0	11.1	12
	µg/l	TY3			7.82		8.68	7.82	7.96	0.51	6.4	4
	µg/l	V4M		0.45	13.2	20	13.8	13.2	12.8	1.4	11.0	11
Se	µg/l	A1M		-0.97	18.5	10	17.6	18.5	18.6	1.5	8.1	12
	µg/l	P2M		-1.17	35.1	20	31.0	35.6	35.1	3.3	9.3	11
	µg/l	TN3		-0.86	13.9	20	12.7	13.6	13.9	1.2	9.0	11
	µg/l	TY3			15.3		14.1	15.3	14.8	2.4	16.5	4
	µg/l	V4M		-0.61	19.8	15	18.9	19.8	19.4	1.7	8.9	11
Sn	µg/l	A1M		-0.80	17.5	10	16.8	16.9	16.8	1.0	5.9	11
	µg/l	P2M		-0.30	8.03	25	7.73	8.00	8.03	0.99	12.4	9
	µg/l	TN3		0.67	33.6	15	35.3	32.8	33.6	2.3	6.8	10
	µg/l	TY3			33.9		35.3	33.9	33.6	1.7	4.9	4
	µg/l	V4M			0.72		0.59	0.72	0.76	0.19	24.7	7
Sr	µg/l	A1M		-0.55	110	10	107	106	106	5	5.1	9
	µg/l	P2M		0.00	200	15	200	200	199	16	7.9	8
	µg/l	TN3		0.00	150	15	150	150	148	9	6.3	10
	µg/l	TY3			150		150	150	150	0	0.1	3
	µg/l	V4M		0.38	79.2	10	80.7	79.2	80.7	3.7	4.5	9
Ti	µg/l	A1M		-1.24	35.5	10	33.3	35.4	35.2	1.6	4.7	10
	µg/l	P2M		-0.15	16.0	25	15.7	16.0	16.2	2.1	13.2	8
	µg/l	TN3		0.00	116	10	116	116	116	4	3.7	10
	µg/l	TY3			125		117	125	123	5	4.0	3
	µg/l	V4M		0.04	50.1	10	50.2	50.1	49.9	1.8	3.7	10

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
V	µg/l	A1M		-0.74	13.5	10	13.0	13.1	13.3	0.8	5.9	10
	µg/l	P2M		-0.65	6.19	20	5.79	6.19	6.35	0.54	8.6	10
	µg/l	TN3		0.00	132	15	132	132	132	4	3.3	9
	µg/l	TY3			138		138	138	142	14	9.8	3
	µg/l	V4M		-0.35	34.6	15	33.7	34.6	34.3	2.0	5.9	10
Zn	µg/l	A1M		-1.61	54.5	10	50.1	53.9	54.7	4.9	9.0	20
	µg/l	P2M		-1.17	21.3	20	18.8	20.4	21.4	2.7	12.8	13
	µg/l	TN3		-1.33	170	15	153	173	169	13	7.8	18
	µg/l	TY3			171		153	171	167	24	14.6	5
	µg/l	V4M		-0.82	42.5	15	39.9	42.4	42.6	2.0	4.6	14

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cr	µg/l	A1M		0.00	15.0	15	15.0	14.5	14.7	1.4	9.5	18
	µg/l	TN3		0.45	13.4	20	14.0	13.5	13.5	1.0	7.6	14
Fe	µg/l	A1M		-0.70	230	10	222	223	223	13	5.8	21
	µg/l	TN3		-0.25	159	15	156	159	159	11	6.7	18
Mo	µg/l	A1M		0.44	22.5	10	23.0	22.4	22.4	1.2	5.3	14
	µg/l	TN3		-1.03	1202	10	1140	1181	1202	55	4.6	11
Ni	µg/l	A1M		-1.71	17.5	10	16.0	17.0	16.9	1.1	6.4	15
	µg/l	TN3		-0.52	28.1	15	27.0	28.0	28.1	2.3	8.1	15
Zn	µg/l	A1M		-0.18	54.5	10	54.0	53.9	54.7	4.9	9.0	20
	µg/l	TN3		-0.24	170	15	167	173	169	13	7.8	18

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-0.35	115	15	112	112	112	12	10.9	13
	µg/l	TN3		-0.32	79.2	20	76.7	79.2	79.3	7.3	9.3	11
	µg/l	V4M		0.00	110	20	110	110	110	10	9.1	10
As	µg/l	A1M		-1.49	55.0	10	50.9	53.2	53.0	2.7	5.2	13
	µg/l	TN3		-1.29	50.2	20	43.7	48.9	50.3	3.9	7.8	13
B	µg/l	A1M		-0.54	85.0	10	82.7	81.2	80.4	6.5	8.1	10
	µg/l	TN3		0.19	157	25	161	157	158	19	12.0	9
	µg/l	V4M		0.42	93.5	20	97.4	92.9	93.5	7.3	7.8	9
Ca	mg/l	A1M		-0.16	33.0	10	32.7	32.8	32.7	0.9	2.7	14
	mg/l	TN3		0.60	65.5	10	67.5	65.8	65.4	1.9	2.9	15
	mg/l	V4M		0.22	33.9	10	34.3	34.0	34.0	1.1	3.2	12
Cd	µg/l	A1M		0.00	4.50	15	4.50	4.47	4.43	0.23	5.2	13
	µg/l	TN3		0.59	9.96	15	10.40	10.00	9.96	0.53	5.3	13
	µg/l	V4M		0.65	6.96	15	7.30	7.08	6.93	0.42	6.1	12
Co	µg/l	A1M		-3.03	11.0	15	8.5	10.5	10.4	0.8	7.6	16
	µg/l	TN3		-2.18	10.1	20	7.9	10.0	10.1	1.1	11.1	13
	µg/l	V4M		-5.44	5.04	20	2.30	4.97	5.04	0.27	5.3	10
Cr	µg/l	A1M		0.36	15.0	15	15.4	14.5	14.7	1.4	9.5	18
	µg/l	TN3		-0.07	13.4	20	13.3	13.5	13.5	1.0	7.6	14
	µg/l	V4M		-0.03	7.82	15	7.80	7.73	7.82	0.56	7.2	12

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cu	µg/l	A1M		0.55	33.0	10	33.9	31.6	31.6	1.7	5.4	18
	µg/l	TN3		0.88	18.1	25	20.1	17.5	18.1	1.9	10.6	15
	µg/l	V4M		2.23	3.05	25	3.9	3.0	3.1	0.4	12.7	13
Fe	µg/l	A1M		0.35	230	10	234	223	223	13	5.8	21
	µg/l	TN3		0.59	159	15	166	159	159	11	6.7	18
	µg/l	V4M		0.27	44.1	15	45.0	43.8	44.3	2.8	6.4	12
K	mg/l	A1M		-0.22	25.0	10	24.7	24.3	24.3	0.6	2.5	12
	mg/l	TN3		0.43	43.8	10	44.7	43.6	43.8	1.0	2.4	10
	mg/l	V4M		0.28	21.8	10	22.1	22.0	21.8	0.6	2.9	12
Mg	mg/l	A1M		-0.25	13.5	10	13.3	13.2	13.2	0.4	3.3	17
	mg/l	TN3		0.52	19.7	10	20.2	19.6	19.6	0.8	3.9	14
	mg/l	V4M		0.14	7.49	10	7.54	7.52	7.49	0.28	3.8	12
Mn	µg/l	A1M		0.74	45.9	10	47.6	44.4	44.6	3.2	7.2	17
	µg/l	TN3		0.71	169	15	178	172	169	12	7.2	16
	µg/l	V4M		0.83	68.7	20	74.4	68.2	68.7	5.0	7.3	12
Ni	µg/l	A1M		-0.23	17.5	10	17.3	17.0	16.9	1.1	6.4	15
	µg/l	TN3		0.71	28.1	15	29.6	28.0	28.1	2.3	8.1	15
	µg/l	V4M		2.44	6.00	15	7.10	6.00	6.01	0.38	6.4	11
Pb	µg/l	TN3		-10.75	30.5	15	5.9	27.4	27.8	3.6	12.8	11
Sr	µg/l	A1M		-0.73	110	10	106	106	106	5	5.1	9
	µg/l	TN3		-0.36	150	15	146	150	148	9	6.3	10
	µg/l	V4M		-0.35	79.2	10	77.8	79.2	80.7	3.7	4.5	9
Zn	µg/l	A1M		0.44	54.5	10	55.7	53.9	54.7	4.9	9.0	20
	µg/l	TN3		0.47	170	15	176	173	169	13	7.8	18
	µg/l	V4M		0.44	42.5	15	43.9	42.4	42.6	2.0	4.6	14

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-1.04	115	15	106	112	112	12	10.9	13
	µg/l	P2M		0.00	202	20	202	202	199	16	8.2	9
	µg/l	TN3		0.00	79.2	20	79.2	79.2	79.3	7.3	9.3	11
	µg/l	V4M		-0.45	110	20	105	110	110	10	9.1	10
As	µg/l	A1M		-2.04	55.0	10	49.4	53.2	53.0	2.7	5.2	13
	µg/l	P2M		-1.54	11.2	20	9.5	11.2	11.1	1.0	9.4	9
	µg/l	TN3		-0.48	50.2	20	47.8	48.9	50.3	3.9	7.8	13
	µg/l	V4M		-0.97	5.35	20	4.83	5.35	5.34	0.33	6.2	10
B	µg/l	A1M		17.88	85.0	10	161.0	81.2	80.4	6.5	8.1	10
	µg/l	P2M		13.08	68.9	20	159.0	68.9	67.2	4.1	6.1	7
	µg/l	TN3		3.31	157	25	222	157	158	19	12.0	9
	µg/l	V4M		6.47	93.5	20	154.0	92.9	93.5	7.3	7.8	9
Ba	µg/l	A1M		-1.38	130	10	121	121	122	7	5.5	11
	µg/l	P2M		-0.40	198	15	192	200	198	14	7.1	9
	µg/l	TN3		-0.38	74.2	15	72.1	74.2	75.1	6.5	8.7	10
	µg/l	V4M		-0.51	62.4	15	60.0	62.4	62.5	4.9	7.9	10
Ca	mg/l	A1M		-1.27	33.0	10	30.9	32.8	32.7	0.9	2.7	14
	mg/l	P2M		0.00	63.8	10	63.8	63.8	63.8	3.1	4.9	11
	mg/l	TN3		-0.52	65.5	10	63.8	65.8	65.4	1.9	2.9	15
	mg/l	V4M		-1.18	33.9	10	31.9	34.0	34.0	1.1	3.2	12

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cd	µg/l	A1M		-0.98	4.50	15	4.17	4.47	4.43	0.23	5.2	13
	µg/l	P2M		-1.33	2.00	15	1.80	2.00	2.00	0.12	5.8	11
	µg/l	TN3		-0.05	9.96	15	9.92	10.00	9.96	0.53	5.3	13
	µg/l	V4M		-1.21	6.96	15	6.33	7.08	6.93	0.42	6.1	12
Co	µg/l	A1M		-0.36	11.0	15	10.7	10.5	10.4	0.8	7.6	16
	µg/l	P2M		0.86	14.0	20	15.2	14.0	14.2	1.4	9.9	11
	µg/l	TN3		1.09	10.1	20	11.2	10.0	10.1	1.1	11.1	13
	µg/l	V4M		0.08	5.04	20	5.08	4.97	5.04	0.27	5.3	10
Cr	µg/l	A1M		-0.67	15.0	15	14.3	14.5	14.7	1.4	9.5	18
	µg/l	P2M		1.26	4.64	15	5.08	4.64	4.73	0.41	8.7	11
	µg/l	TN3		0.25	13.4	20	13.7	13.5	13.5	1.0	7.6	14
	µg/l	V4M		0.53	7.82	15	8.13	7.73	7.82	0.56	7.2	12
Cu	µg/l	A1M		-0.21	33.0	10	32.7	31.6	31.6	1.7	5.4	18
	µg/l	P2M		1.17	21.1	20	23.6	21.0	21.2	1.8	8.5	13
	µg/l	TN3		0.23	18.1	25	18.6	17.5	18.1	1.9	10.6	15
	µg/l	V4M		0.45	3.05	25	3.2	3.0	3.1	0.4	12.7	13
Fe	µg/l	A1M		-0.35	230	10	226	223	223	13	5.8	21
	µg/l	P2M		0.07	84.9	25	85.6	84.9	83.9	11.0	13.1	11
	µg/l	TN3		0.42	159	15	164	159	159	11	6.7	18
	µg/l	V4M		0.60	44.1	15	46.1	43.8	44.3	2.8	6.4	12
Hg	µg/l	A1Hg		2.74	0.84	20	1.07	0.83	0.85	0.11	13.1	13
	µg/l	P2Hg		0.98	0.44	20	0.48	0.44	0.46	0.06	12.8	11
	µg/l	T3Hg		0.72	3.47	20	3.72	3.39	3.43	0.34	10.0	14
	µg/l	V4Hg			2.29		3.06	2.29	2.10	0.52	24.8	9
K	mg/l	A1M		-1.12	25.0	10	23.6	24.3	24.3	0.6	2.5	12
	mg/l	P2M		-0.07	36.1	10	36.0	36.0	36.1	1.2	3.4	10
	mg/l	TN3		-0.23	43.8	10	43.3	43.6	43.8	1.0	2.4	10
	mg/l	V4M		-0.60	21.8	10	21.2	22.0	21.8	0.6	2.9	12
Mg	mg/l	A1M		-1.63	13.5	10	12.4	13.2	13.2	0.4	3.3	17
	mg/l	P2M		-0.44	11.9	10	11.6	11.9	11.8	0.2	2.0	10
	mg/l	TN3		-0.53	19.7	10	19.2	19.6	19.6	0.8	3.9	14
	mg/l	V4M		-1.04	7.49	10	7.10	7.52	7.49	0.28	3.8	12
Mn	µg/l	A1M		-0.66	45.9	10	44.4	44.4	44.6	3.2	7.2	17
	µg/l	P2M		0.65	18.0	20	19.2	18.0	18.4	2.2	12.1	11
	µg/l	TN3		0.24	169	15	172	172	169	12	7.2	16
	µg/l	V4M		0.00	68.7	20	68.7	68.2	68.7	5.0	7.3	12
Mo	µg/l	A1M		-0.53	22.5	10	21.9	22.4	22.4	1.2	5.3	14
	µg/l	P2M		-0.89	6.20	20	5.65	6.20	6.18	0.65	10.4	10
	µg/l	TN3		-0.53	1202	10	1170	1181	1202	55	4.6	11
	µg/l	V4M		1.30	12.3	20	13.9	12.3	12.6	1.3	10.1	9
Ni	µg/l	A1M		-0.11	17.5	10	17.4	17.0	16.9	1.1	6.4	15
	µg/l	P2M		1.90	10.5	15	12.0	10.5	10.8	0.9	8.4	11
	µg/l	TN3		0.76	28.1	15	29.7	28.0	28.1	2.3	8.1	15
	µg/l	V4M		1.04	6.00	15	6.47	6.00	6.01	0.38	6.4	11
Pb	µg/l	A1M		-0.21	18.8	10	18.6	17.6	17.3	1.7	9.9	13
	µg/l	P2M		0.27	10.0	15	10	9	9	1	15.0	11
	µg/l	TN3		-0.66	30.5	15	29.0	27.4	27.8	3.6	12.8	11
	µg/l	V4M		-0.03	3.15	20	3.14	2.79	2.78	0.39	14.0	11

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Sb	µg/l	A1M		-0.18	33.0	10	32.7	31.7	31.7	2.0	6.4	12
	µg/l	P2M		-0.63	25.5	15	24.3	25.5	25.6	1.8	7.0	11
	µg/l	TN3		0.77	9.2	20	9.9	8.9	9.2	1.0	11.1	12
	µg/l	V4M		-0.61	13.2	20	12.4	13.2	12.8	1.4	11.0	11
Se	µg/l	A1M		-0.54	18.5	10	18.0	18.5	18.6	1.5	8.1	12
	µg/l	P2M		-0.91	35.1	20	31.9	35.6	35.1	3.3	9.3	11
	µg/l	TN3		-0.50	13.9	20	13.2	13.6	13.9	1.2	9.0	11
	µg/l	V4M		-1.35	19.8	15	17.8	19.8	19.4	1.7	8.9	11
Sn	µg/l	A1M		-0.34	17.5	10	17.2	16.9	16.8	1.0	5.9	11
	µg/l	P2M		0.33	8.03	25	8.36	8.00	8.03	0.99	12.4	9
	µg/l	TN3		0.67	33.6	15	35.3	32.8	33.6	2.3	6.8	10
	µg/l	V4M			0.72		0.97	0.72	0.76	0.19	24.7	7
Sr	µg/l	A1M		-0.73	110	10	106	106	106	5	5.1	9
	µg/l	P2M		0.40	200	15	206	200	199	16	7.9	8
	µg/l	TN3		0.09	150	15	151	150	148	9	6.3	10
	µg/l	V4M		0.25	79.2	10	80.2	79.2	80.7	3.7	4.5	9
Ti	µg/l	A1M		-0.39	35.5	10	34.8	35.4	35.2	1.6	4.7	10
	µg/l	P2M		-0.10	16.0	25	15.8	16.0	16.2	2.1	13.2	8
	µg/l	TN3		0.00	116	10	116	116	116	4	3.7	10
	µg/l	V4M		-0.76	50.1	10	48.2	50.1	49.9	1.8	3.7	10
V	µg/l	A1M		-1.33	13.5	10	12.6	13.1	13.3	0.8	5.9	10
	µg/l	P2M		-0.16	6.19	20	6.09	6.19	6.35	0.54	8.6	10
	µg/l	TN3		-0.51	132	15	127	132	132	4	3.3	9
	µg/l	V4M		-0.73	34.6	15	32.7	34.6	34.3	2.0	5.9	10
Zn	µg/l	A1M		-0.48	54.5	10	53.2	53.9	54.7	4.9	9.0	20
	µg/l	P2M		0.52	21.3	20	22.4	20.4	21.4	2.7	12.8	13
	µg/l	TN3		0.24	170	15	173	173	169	13	7.8	18
	µg/l	V4M		0.06	42.5	15	42.7	42.4	42.6	2.0	4.6	14

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-0.58	115	15	110	112	112	12	10.9	13
	µg/l	P2M		-0.35	202	20	195	202	199	16	8.2	9
	µg/l	TN3		-0.40	79.2	20	76.0	79.2	79.3	7.3	9.3	11
	µg/l	V4M		0.23	110	20	113	110	110	10	9.1	10
As	µg/l	A1M		-0.01	55.0	10	55.0	53.2	53.0	2.7	5.2	13
	µg/l	P2M		0.63	11.2	20	11.9	11.2	11.1	1.0	9.4	9
	µg/l	TN3		-0.26	50.2	20	48.9	48.9	50.3	3.9	7.8	13
	µg/l	V4M		0.43	5.35	20	5.58	5.35	5.34	0.33	6.2	10
B	µg/l	A1M		-0.32	85.0	10	83.6	81.2	80.4	6.5	8.1	10
	µg/l	P2M		0.30	68.9	20	71.0	68.9	67.2	4.1	6.1	7
	µg/l	TN3		-0.29	157	25	151	157	158	19	12.0	9
	µg/l	V4M		-0.06	93.5	20	92.9	92.9	93.5	7.3	7.8	9
Ba	µg/l	A1M		-0.06	130	10	130	121	122	7	5.5	11
	µg/l	P2M		1.39	198	15	219	200	198	14	7.1	9
	µg/l	TN3		1.64	74.2	15	83.3	74.2	75.1	6.5	8.7	10
	µg/l	V4M		1.67	62.4	15	70.2	62.4	62.5	4.9	7.9	10

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ca	mg/l	A1M		-0.10	33.0	10	32.8	32.8	32.7	0.9	2.7	14
	mg/l	P2M		-0.07	63.8	10	63.6	63.8	63.8	3.1	4.9	11
	mg/l	TN3		0.09	65.5	10	65.8	65.8	65.4	1.9	2.9	15
	mg/l	V4M		-0.32	33.9	10	33.4	34.0	34.0	1.1	3.2	12
Cd	µg/l	A1M		-0.33	4.50	15	4.39	4.47	4.43	0.23	5.2	13
	µg/l	P2M		-0.13	2.00	15	1.98	2.00	2.00	0.12	5.8	11
	µg/l	TN3		-0.44	9.96	15	9.63	10.00	9.96	0.53	5.3	13
	µg/l	V4M		0.61	6.96	15	7.28	7.08	6.93	0.42	6.1	12
Co	µg/l	A1M		0.00	11.0	15	11.0	10.5	10.4	0.8	7.6	16
	µg/l	P2M		1.52	14.0	20	16.1	14.0	14.2	1.4	9.9	11
	µg/l	TN3		-1.09	10.1	20	9.0	10.0	10.1	1.1	11.1	13
	µg/l	V4M		0.60	5.04	20	5.34	4.97	5.04	0.27	5.3	10
Cr	µg/l	A1M		-0.56	15.0	15	14.4	14.5	14.7	1.4	9.5	18
	µg/l	P2M		0.00	4.64	15	4.64	4.64	4.73	0.41	8.7	11
	µg/l	TN3		-0.97	13.4	20	12.1	13.5	13.5	1.0	7.6	14
	µg/l	V4M		-0.27	7.82	15	7.66	7.73	7.82	0.56	7.2	12
Cu	µg/l	A1M		-0.80	33.0	10	31.7	31.6	31.6	1.7	5.4	18
	µg/l	P2M		0.38	21.1	20	21.9	21.0	21.2	1.8	8.5	13
	µg/l	TN3		-0.44	18.1	25	17.1	17.5	18.1	1.9	10.6	15
	µg/l	V4M		0.21	3.05	25	3.1	3.0	3.1	0.4	12.7	13
Fe	µg/l	A1M		-0.50	230	10	224	223	223	13	5.8	21
	µg/l	P2M		0.40	84.9	25	89.1	84.9	83.9	11.0	13.1	11
	µg/l	TN3		-0.86	159	15	149	159	159	11	6.7	18
	µg/l	V4M		0.63	44.1	15	46.2	43.8	44.3	2.8	6.4	12
Hg	µg/l	A1Hg		-0.20	0.84	20	0.82	0.83	0.85	0.11	13.1	13
	µg/l	P2Hg		-0.45	0.44	20	0.42	0.44	0.46	0.06	12.8	11
	µg/l	T3Hg		-0.20	3.47	20	3.40	3.39	3.43	0.34	10.0	14
	µg/l	V4Hg			2.29		1.53	2.29	2.10	0.52	24.8	9
K	mg/l	A1M		-0.25	25.0	10	24.7	24.3	24.3	0.6	2.5	12
	mg/l	P2M		1.51	36.1	10	38.8	36.0	36.1	1.2	3.4	10
	mg/l	TN3		0.75	43.8	10	45.5	43.6	43.8	1.0	2.4	10
	mg/l	V4M		0.35	21.8	10	22.2	22.0	21.8	0.6	2.9	12
Mg	mg/l	A1M		-0.43	13.5	10	13.2	13.2	13.2	0.4	3.3	17
	mg/l	P2M		-0.49	11.9	10	11.6	11.9	11.8	0.2	2.0	10
	mg/l	TN3		-0.31	19.7	10	19.4	19.6	19.6	0.8	3.9	14
	mg/l	V4M		-0.24	7.49	10	7.40	7.52	7.49	0.28	3.8	12
Mn	µg/l	A1M		0.39	45.9	10	46.8	44.4	44.6	3.2	7.2	17
	µg/l	P2M		1.61	18.0	20	20.9	18.0	18.4	2.2	12.1	11
	µg/l	TN3		-0.95	169	15	157	172	169	12	7.2	16
	µg/l	V4M		0.84	68.7	20	74.5	68.2	68.7	5.0	7.3	12
Mo	µg/l	A1M		1.46	22.5	10	24.1	22.4	22.4	1.2	5.3	14
	µg/l	P2M		1.60	6.20	20	7.19	6.20	6.18	0.65	10.4	10
	µg/l	TN3		1.38	1202	10	1285	1181	1202	55	4.6	11
	µg/l	V4M		0.89	12.3	20	13.4	12.3	12.6	1.3	10.1	9
Ni	µg/l	A1M		0.02	17.5	10	17.5	17.0	16.9	1.1	6.4	15
	µg/l	P2M		1.61	10.5	15	11.8	10.5	10.8	0.9	8.4	11
	µg/l	TN3		1.33	28.1	15	30.9	28.0	28.1	2.3	8.1	15
	µg/l	V4M		0.93	6.00	15	6.42	6.00	6.01	0.38	6.4	11

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Pb	µg/l	A1M		0.02	18.8	10	18.8	17.6	17.3	1.7	9.9	13
	µg/l	P2M		1.67	10.0	15	11	9	9	1	15.0	11
	µg/l	TN3		-1.57	30.5	15	26.9	27.4	27.8	3.6	12.8	11
	µg/l	V4M		0.41	3.15	20	3.28	2.79	2.78	0.39	14.0	11
Sb	µg/l	A1M		-1.41	33.0	10	30.7	31.7	31.7	2.0	6.4	12
	µg/l	P2M		0.83	25.5	15	27.1	25.5	25.6	1.8	7.0	11
	µg/l	TN3		-0.08	9.2	20	9.1	8.9	9.2	1.0	11.1	12
	µg/l	V4M		0.02	13.2	20	13.2	13.2	12.8	1.4	11.0	11
Se	µg/l	A1M		-0.02	18.5	10	18.5	18.5	18.6	1.5	8.1	12
	µg/l	P2M		0.50	35.1	20	36.9	35.6	35.1	3.3	9.3	11
	µg/l	TN3		0.71	13.9	20	14.9	13.6	13.9	1.2	9.0	11
	µg/l	V4M		0.48	19.8	15	20.5	19.8	19.4	1.7	8.9	11
Sn	µg/l	A1M		-0.01	17.5	10	17.5	16.9	16.8	1.0	5.9	11
	µg/l	P2M		1.99	8.03	25	10.03	8.00	8.03	0.99	12.4	9
	µg/l	TN3		-0.95	33.6	15	31.2	32.8	33.6	2.3	6.8	10
	µg/l	V4M			0.72		0.72	0.72	0.76	0.19	24.7	7
Sr	µg/l	A1M		1.09	110	10	116	106	106	5	5.1	9
	µg/l	P2M		2.33	200	15	235	200	199	16	7.9	8
	µg/l	TN3		-0.02	150	15	150	150	148	9	6.3	10
	µg/l	V4M		2.22	79.2	10	88.0	79.2	80.7	3.7	4.5	9
Ti	µg/l	A1M		-0.96	35.5	10	33.8	35.4	35.2	1.6	4.7	10
	µg/l	P2M			16.0	25	*<15*	16.0	16.2	2.1	13.2	8
	µg/l	TN3		0.17	116	10	117	116	116	4	3.7	10
	µg/l	V4M		-1.24	50.1	10	47.0	50.1	49.9	1.8	3.7	10
V	µg/l	A1M		-0.31	13.5	10	13.3	13.1	13.3	0.8	5.9	10
	µg/l	P2M		0.36	6.19	20	6.41	6.19	6.35	0.54	8.6	10
	µg/l	TN3		0.00	132	15	132	132	132	4	3.3	9
	µg/l	V4M		0.03	34.6	15	34.7	34.6	34.3	2.0	5.9	10
Zn	µg/l	A1M		-0.79	54.5	10	52.3	53.9	54.7	4.9	9.0	20
	µg/l	P2M		-0.60	21.3	20	20.0	20.4	21.4	2.7	12.8	13
	µg/l	TN3		-0.71	170	15	161	173	169	13	7.8	18
	µg/l	V4M		-0.03	42.5	15	42.4	42.4	42.6	2.0	4.6	14

Participant 20												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-4.86	115	15	73	112	112	12	10.9	13
	µg/l	P2M		-2.38	202	20	154	202	199	16	8.2	9
	µg/l	TN3		0.77	79.2	20	85.3	79.2	79.3	7.3	9.3	11
	µg/l	V4M		-3.85	110	20	68	110	110	10	9.1	10
B	µg/l	A1M		-3.04	85.0	10	72.1	81.2	80.4	6.5	8.1	10
	µg/l	P2M		-1.03	68.9	20	61.8	68.9	67.2	4.1	6.1	7
	µg/l	TN3		-1.02	157	25	137	157	158	19	12.0	9
	µg/l	V4M		-1.20	93.5	20	82.3	92.9	93.5	7.3	7.8	9
Ca	mg/l	A1M		0.79	33.0	10	34.3	32.8	32.7	0.9	2.7	14
	mg/l	P2M		-1.41	63.8	10	59.3	63.8	63.8	3.1	4.9	11
	mg/l	TN3		-0.70	65.5	10	63.2	65.8	65.4	1.9	2.9	15
	mg/l	V4M		0.71	33.9	10	35.1	34.0	34.0	1.1	3.2	12

Participant 20												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Cu	µg/l	A1M		-0.85	33.0	10	31.6	31.6	31.6	1.7	5.4	18
	µg/l	P2M		0.38	21.1	20	21.9	21.0	21.2	1.8	8.5	13
	µg/l	TN3		0.31	18.1	25	18.8	17.5	18.1	1.9	10.6	15
	µg/l	V4M		-1.44	3.05	25	2.5	3.0	3.1	0.4	12.7	13
Fe	µg/l	A1M		1.57	230	10	248	223	223	13	5.8	21
	µg/l	P2M		1.52	84.9	25	101.0	84.9	83.9	11.0	13.1	11
	µg/l	TN3		0.75	159	15	168	159	159	11	6.7	18
	µg/l	V4M		9.83	44.1	15	76.6	43.8	44.3	2.8	6.4	12
K	mg/l	A1M		-0.96	25.0	10	23.8	24.3	24.3	0.6	2.5	12
	mg/l	P2M		-0.61	36.1	10	35.0	36.0	36.1	1.2	3.4	10
	mg/l	TN3		-0.55	43.8	10	42.6	43.6	43.8	1.0	2.4	10
	mg/l	V4M		-0.64	21.8	10	21.1	22.0	21.8	0.6	2.9	12
Mg	mg/l	A1M		-0.44	13.5	10	13.2	13.2	13.2	0.4	3.3	17
	mg/l	P2M		-0.84	11.9	10	11.4	11.9	11.8	0.2	2.0	10
	mg/l	TN3		-0.30	19.7	10	19.4	19.6	19.6	0.8	3.9	14
	mg/l	V4M		-0.32	7.49	10	7.37	7.52	7.49	0.28	3.8	12
Mn	µg/l	A1M		1.83	45.9	10	50.1	44.4	44.6	3.2	7.2	17
	µg/l	P2M		1.78	18.0	20	21.2	18.0	18.4	2.2	12.1	11
	µg/l	TN3		0.63	169	15	177	172	169	12	7.2	16
	µg/l	V4M		0.99	68.7	20	75.5	68.2	68.7	5.0	7.3	12
Mo	µg/l	A1M		0.53	22.5	10	23.1	22.4	22.4	1.2	5.3	14
	µg/l	P2M		0.48	6.20	20	6.50	6.20	6.18	0.65	10.4	10
	µg/l	TN3		-2.20	1202	10	1070	1181	1202	55	4.6	11
	µg/l	V4M		15.37	12.3	20	31.2	12.3	12.6	1.3	10.1	9
Zn	µg/l	A1M		0.92	54.5	10	57.0	53.9	54.7	4.9	9.0	20
	µg/l	P2M		0.28	21.3	20	21.9	20.4	21.4	2.7	12.8	13
	µg/l	TN3		0.39	170	15	175	173	169	13	7.8	18
	µg/l	V4M		0.78	42.5	15	45.0	42.4	42.6	2.0	4.6	14

Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		-0.58	115	15	110	112	112	12	10.9	13
	µg/l	P2M		1.39	202	20	230	202	199	16	8.2	9
	µg/l	TN3		0.98	79.2	20	87.0	79.2	79.3	7.3	9.3	11
	µg/l	V4M		0.91	110	20	120	110	110	10	9.1	10
As	µg/l	A1M		-0.36	55.0	10	54.0	53.2	53.0	2.7	5.2	13
	µg/l	P2M		0.71	11.2	20	12.0	11.2	11.1	1.0	9.4	9
	µg/l	TN3		1.55	50.2	20	58.0	48.9	50.3	3.9	7.8	13
	µg/l	V4M		0.47	5.35	20	5.60	5.35	5.34	0.33	6.2	10
B	µg/l	A1M		-2.59	85.0	10	74.0	81.2	80.4	6.5	8.1	10
	µg/l	P2M		-1.15	68.9	20	61.0	68.9	67.2	4.1	6.1	7
	µg/l	TN3		0.66	157	25	170	157	158	19	12.0	9
	µg/l	V4M		-0.91	93.5	20	85.0	92.9	93.5	7.3	7.8	9
Ba	µg/l	A1M		-1.54	130	10	120	121	122	7	5.5	11
	µg/l	P2M		-1.21	198	15	180	200	198	14	7.1	9
	µg/l	TN3		-0.22	74.2	15	73.0	74.2	75.1	6.5	8.7	10
	µg/l	V4M		-0.94	62.4	15	58.0	62.4	62.5	4.9	7.9	10

Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Ca	mg/l	A1M		0.00	33.0	10	33.0	32.8	32.7	0.9	2.7	14
	mg/l	P2M		-0.25	63.8	10	63.0	63.8	63.8	3.1	4.9	11
	mg/l	TN3		-0.46	65.5	10	64.0	65.8	65.4	1.9	2.9	15
	mg/l	V4M		0.06	33.9	10	34.0	34.0	34.0	1.1	3.2	12
Cd	µg/l	A1M		-0.89	4.50	15	4.20	4.47	4.43	0.23	5.2	13
	µg/l	P2M		0.00	2.00	15	2.00	2.00	2.00	0.12	5.8	11
	µg/l	TN3		0.05	9.96	15	10.00	10.00	9.96	0.53	5.3	13
	µg/l	V4M		-0.50	6.96	15	6.70	7.08	6.93	0.42	6.1	12
Co	µg/l	A1M		-1.45	11.0	15	9.8	10.5	10.4	0.8	7.6	16
	µg/l	P2M		0.00	14.0	20	14.0	14.0	14.2	1.4	9.9	11
	µg/l	TN3		-0.10	10.1	20	10.0	10.0	10.1	1.1	11.1	13
	µg/l	V4M		-0.48	5.04	20	4.80	4.97	5.04	0.27	5.3	10
Cr	µg/l	A1M		0.00	15.0	15	15.0	14.5	14.7	1.4	9.5	18
	µg/l	P2M		1.32	4.64	15	5.10	4.64	4.73	0.41	8.7	11
	µg/l	TN3		1.19	13.4	20	15.0	13.5	13.5	1.0	7.6	14
	µg/l	V4M		1.16	7.82	15	8.50	7.73	7.82	0.56	7.2	12
Cu	µg/l	A1M		-2.42	33.0	10	29.0	31.6	31.6	1.7	5.4	18
	µg/l	P2M		-0.05	21.1	20	21.0	21.0	21.2	1.8	8.5	13
	µg/l	TN3		-0.49	18.1	25	17.0	17.5	18.1	1.9	10.6	15
	µg/l	V4M		-0.39	3.05	25	2.9	3.0	3.1	0.4	12.7	13
Fe	µg/l	A1M		-0.52	230	10	224	223	223	13	5.8	21
	µg/l	P2M		-0.18	84.9	25	83.0	84.9	83.9	11.0	13.1	11
	µg/l	TN3		-0.17	159	15	157	159	159	11	6.7	18
	µg/l	V4M		-0.03	44.1	15	44.0	43.8	44.3	2.8	6.4	12
Hg	µg/l	A1Hg		0.12	0.84	20	0.85	0.83	0.85	0.11	13.1	13
	µg/l	P2Hg		-0.68	0.44	20	0.41	0.44	0.46	0.06	12.8	11
	µg/l	T3Hg		0.95	3.47	20	3.80	3.39	3.43	0.34	10.0	14
	µg/l	V4Hg			2.29		2.10	2.29	2.10	0.52	24.8	9
K	mg/l	A1M		0.00	25.0	10	25.0	24.3	24.3	0.6	2.5	12
	mg/l	P2M		-0.06	36.1	10	36.0	36.0	36.1	1.2	3.4	10
	mg/l	TN3		-0.37	43.8	10	43.0	43.6	43.8	1.0	2.4	10
	mg/l	V4M		0.18	21.8	10	22.0	22.0	21.8	0.6	2.9	12
Mg	mg/l	A1M		-0.74	13.5	10	13.0	13.2	13.2	0.4	3.3	17
	mg/l	P2M		0.17	11.9	10	12.0	11.9	11.8	0.2	2.0	10
	mg/l	TN3		-0.71	19.7	10	19.0	19.6	19.6	0.8	3.9	14
	mg/l	V4M		-0.51	7.49	10	7.30	7.52	7.49	0.28	3.8	12
Mn	µg/l	A1M		-2.14	45.9	10	41.0	44.4	44.6	3.2	7.2	17
	µg/l	P2M		0.00	18.0	20	18.0	18.0	18.4	2.2	12.1	11
	µg/l	TN3		0.08	169	15	170	172	169	12	7.2	16
	µg/l	V4M		-0.39	68.7	20	66.0	68.2	68.7	5.0	7.3	12
Mo	µg/l	A1M		1.33	22.5	10	24.0	22.4	22.4	1.2	5.3	14
	µg/l	P2M		0.65	6.20	20	6.60	6.20	6.18	0.65	10.4	10
	µg/l	TN3		1.63	1202	10	1300	1181	1202	55	4.6	11
	µg/l	V4M		0.57	12.3	20	13.0	12.3	12.6	1.3	10.1	9
Ni	µg/l	A1M		-1.71	17.5	10	16.0	17.0	16.9	1.1	6.4	15
	µg/l	P2M		0.63	10.5	15	11.0	10.5	10.8	0.9	8.4	11
	µg/l	TN3		-0.05	28.1	15	28.0	28.0	28.1	2.3	8.1	15
	µg/l	V4M		-0.22	6.00	15	5.90	6.00	6.01	0.38	6.4	11

Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Pb	µg/l	A1M		-2.98	18.8	10	16.0	17.6	17.3	1.7	9.9	13
	µg/l	P2M		-1.60	10.0	15	9	9	9	1	15.0	11
	µg/l	TN3		-1.53	30.5	15	27.0	27.4	27.8	3.6	12.8	11
	µg/l	V4M		-2.06	3.15	20	2.50	2.79	2.78	0.39	14.0	11
Sb	µg/l	A1M		0.61	33.0	10	34.0	31.7	31.7	2.0	6.4	12
	µg/l	P2M		1.83	25.5	15	29.0	25.5	25.6	1.8	7.0	11
	µg/l	TN3		1.96	9.2	20	11.0	8.9	9.2	1.0	11.1	12
	µg/l	V4M		0.61	13.2	20	14.0	13.2	12.8	1.4	11.0	11
Se	µg/l	A1M		-0.54	18.5	10	18.0	18.5	18.6	1.5	8.1	12
	µg/l	P2M		-0.03	35.1	20	35.0	35.6	35.1	3.3	9.3	11
	µg/l	TN3		0.79	13.9	20	15.0	13.6	13.9	1.2	9.0	11
	µg/l	V4M		0.13	19.8	15	20.0	19.8	19.4	1.7	8.9	11
Sn	µg/l	A1M		-0.57	17.5	10	17.0	16.9	16.8	1.0	5.9	11
	µg/l	P2M		-1.13	8.03	25	6.90	8.00	8.03	0.99	12.4	9
	µg/l	TN3		1.35	33.6	15	37.0	32.8	33.6	2.3	6.8	10
	µg/l	V4M			0.72		*<0,1*	0.72	0.76	0.19	24.7	7
Ti	µg/l	A1M		0.28	35.5	10	36.0	35.4	35.2	1.6	4.7	10
	µg/l	P2M		-1.50	16.0	25	13.0	16.0	16.2	2.1	13.2	8
	µg/l	TN3		-1.03	116	10	110	116	116	4	3.7	10
	µg/l	V4M		-0.04	50.1	10	50.0	50.1	49.9	1.8	3.7	10
V	µg/l	A1M		-0.74	13.5	10	13.0	13.1	13.3	0.8	5.9	10
	µg/l	P2M		0.34	6.19	20	6.40	6.19	6.35	0.54	8.6	10
	µg/l	TN3		-0.20	132	15	130	132	132	4	3.3	9
	µg/l	V4M		0.15	34.6	15	35.0	34.6	34.3	2.0	5.9	10
Zn	µg/l	A1M		-1.28	54.5	10	51.0	53.9	54.7	4.9	9.0	20
	µg/l	P2M		0.33	21.3	20	22.0	20.4	21.4	2.7	12.8	13
	µg/l	TN3		0.78	170	15	180	173	169	13	7.8	18
	µg/l	V4M		-0.16	42.5	15	42.0	42.4	42.6	2.0	4.6	14

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Hg	µg/l	A1Hg		1.86	0.84	20	1.00	0.83	0.85	0.11	13.1	13
	µg/l	P2Hg		-0.20	0.44	20	0.43	0.44	0.46	0.06	12.8	11
	µg/l	T3Hg		0.94	3.47	20	3.80	3.39	3.43	0.34	10.0	14
	µg/l	V4Hg			2.29		1.52	2.29	2.10	0.52	24.8	9

Participant 23												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
Al	µg/l	A1M		0.12	115	15	116	112	112	12	10.9	13
	µg/l	P2M		0.45	202	20	211	202	199	16	8.2	9
	µg/l	TN3		0.34	79.2	20	81.9	79.2	79.3	7.3	9.3	11
	µg/l	V4M		0.45	110	20	115	110	110	10	9.1	10
As	µg/l	A1M		-0.25	55.0	10	54.3	53.2	53.0	2.7	5.2	13
	µg/l	P2M		0.00	11.2	20	11.2	11.2	11.1	1.0	9.4	9
	µg/l	TN3		0.56	50.2	20	53.0	48.9	50.3	3.9	7.8	13
	µg/l	V4M		-0.11	5.35	20	5.29	5.35	5.34	0.33	6.2	10

Participant 23												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
B	µg/l	A1M		-0.75	85.0	10	81.8	81.2	80.4	6.5	8.1	10
	µg/l	P2M		0.23	68.9	20	70.5	68.9	67.2	4.1	6.1	7
	µg/l	TN3		0.00	157	25	157	157	158	19	12.0	9
	µg/l	V4M		0.47	93.5	20	97.9	92.9	93.5	7.3	7.8	9
Ba	µg/l	A1M		-0.92	130	10	124	121	122	7	5.5	11
	µg/l	P2M		0.27	198	15	202	200	198	14	7.1	9
	µg/l	TN3		0.83	74.2	15	78.8	74.2	75.1	6.5	8.7	10
	µg/l	V4M		0.34	62.4	15	64.0	62.4	62.5	4.9	7.9	10
Ca	mg/l	A1M		-0.18	33.0	10	32.7	32.8	32.7	0.9	2.7	14
	mg/l	P2M		0.25	63.8	10	64.6	63.8	63.8	3.1	4.9	11
	mg/l	TN3		0.34	65.5	10	66.6	65.8	65.4	1.9	2.9	15
	mg/l	V4M		0.12	33.9	10	34.1	34.0	34.0	1.1	3.2	12
Cd	µg/l	A1M		-0.09	4.50	15	4.47	4.47	4.43	0.23	5.2	13
	µg/l	P2M		0.87	2.00	15	2.13	2.00	2.00	0.12	5.8	11
	µg/l	TN3		1.26	9.96	15	10.90	10.00	9.96	0.53	5.3	13
	µg/l	V4M		0.63	6.96	15	7.29	7.08	6.93	0.42	6.1	12
Co	µg/l	A1M		-0.61	11.0	15	10.5	10.5	10.4	0.8	7.6	16
	µg/l	P2M		-0.36	14.0	20	13.5	14.0	14.2	1.4	9.9	11
	µg/l	TN3		0.59	10.1	20	10.7	10.0	10.1	1.1	11.1	13
	µg/l	V4M		0.00	5.04	20	5.04	4.97	5.04	0.27	5.3	10
Cr	µg/l	A1M		-0.36	15.0	15	14.6	14.5	14.7	1.4	9.5	18
	µg/l	P2M		-0.49	4.64	15	4.47	4.64	4.73	0.41	8.7	11
	µg/l	TN3		0.07	13.4	20	13.5	13.5	13.5	1.0	7.6	14
	µg/l	V4M		0.22	7.82	15	7.95	7.73	7.82	0.56	7.2	12
Cu	µg/l	A1M		-1.03	33.0	10	31.3	31.6	31.6	1.7	5.4	18
	µg/l	P2M		-0.47	21.1	20	20.1	21.0	21.2	1.8	8.5	13
	µg/l	TN3		-0.44	18.1	25	17.1	17.5	18.1	1.9	10.6	15
	µg/l	V4M		0.16	3.05	25	3.1	3.0	3.1	0.4	12.7	13
Fe	µg/l	A1M		-0.35	230	10	226	223	223	13	5.8	21
	µg/l	P2M		0.53	84.9	25	90.5	84.9	83.9	11.0	13.1	11
	µg/l	TN3		0.92	159	15	170	159	159	11	6.7	18
	µg/l	V4M		0.70	44.1	15	46.4	43.8	44.3	2.8	6.4	12
Hg	µg/l	A1Hg		-0.14	0.84	20	0.83	0.83	0.85	0.11	13.1	13
	µg/l	P2Hg		-0.07	0.44	20	0.44	0.44	0.46	0.06	12.8	11
	µg/l	T3Hg		0.03	3.47	20	3.48	3.39	3.43	0.34	10.0	14
	µg/l	V4Hg			2.29		2.31	2.29	2.10	0.52	24.8	9
K	mg/l	A1M		0.16	25.0	10	25.2	24.3	24.3	0.6	2.5	12
	mg/l	P2M		0.22	36.1	10	36.5	36.0	36.1	1.2	3.4	10
	mg/l	TN3		0.59	43.8	10	45.1	43.6	43.8	1.0	2.4	10
	mg/l	V4M		0.28	21.8	10	22.1	22.0	21.8	0.6	2.9	12
Mg	mg/l	A1M		0.30	13.5	10	13.7	13.2	13.2	0.4	3.3	17
	mg/l	P2M		0.17	11.9	10	12.0	11.9	11.8	0.2	2.0	10
	mg/l	TN3		0.91	19.7	10	20.6	19.6	19.6	0.8	3.9	14
	mg/l	V4M		0.77	7.49	10	7.78	7.52	7.49	0.28	3.8	12
Mn	µg/l	A1M		-0.52	45.9	10	44.7	44.4	44.6	3.2	7.2	17
	µg/l	P2M		0.67	18.0	20	19.2	18.0	18.4	2.2	12.1	11
	µg/l	TN3		0.47	169	15	175	172	169	12	7.2	16

Participant 23												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n_{stat}
	µg/l	V4M		0.12	68.7	20	69.5	68.2	68.7	5.0	7.3	12
Mo	µg/l	A1M		0.53	22.5	10	23.1	22.4	22.4	1.2	5.3	14
	µg/l	P2M		-1.00	6.20	20	5.58	6.20	6.18	0.65	10.4	10
	µg/l	TN3		1.05	1202	10	1265	1181	1202	55	4.6	11
	µg/l	V4M		-0.24	12.3	20	12.0	12.3	12.6	1.3	10.1	9
Ni	µg/l	A1M		-0.57	17.5	10	17.0	17.0	16.9	1.1	6.4	15
	µg/l	P2M		-0.63	10.5	15	10.0	10.5	10.8	0.9	8.4	11
	µg/l	TN3		-0.14	28.1	15	27.8	28.0	28.1	2.3	8.1	15
	µg/l	V4M		0.24	6.00	15	6.11	6.00	6.01	0.38	6.4	11
Pb	µg/l	A1M		-0.11	18.8	10	18.7	17.6	17.3	1.7	9.9	13
	µg/l	P2M		-0.40	10.0	15	10	9	9	1	15.0	11
	µg/l	TN3		0.00	30.5	15	30.5	27.4	27.8	3.6	12.8	11
	µg/l	V4M		-0.10	3.15	20	3.12	2.79	2.78	0.39	14.0	11
Sb	µg/l	A1M		0.00	33.0	10	33.0	31.7	31.7	2.0	6.4	12
	µg/l	P2M		0.99	25.5	15	27.4	25.5	25.6	1.8	7.0	11
	µg/l	TN3		-0.01	9.2	20	9.2	8.9	9.2	1.0	11.1	12
	µg/l	V4M		0.91	13.2	20	14.4	13.2	12.8	1.4	11.0	11
Se	µg/l	A1M		0.54	18.5	10	19.0	18.5	18.6	1.5	8.1	12
	µg/l	P2M		0.23	35.1	20	35.9	35.6	35.1	3.3	9.3	11
	µg/l	TN3		0.29	13.9	20	14.3	13.6	13.9	1.2	9.0	11
	µg/l	V4M		-0.07	19.8	15	19.7	19.8	19.4	1.7	8.9	11
Sn	µg/l	A1M		0.00	17.5	10	17.5	16.9	16.8	1.0	5.9	11
	µg/l	P2M		0.10	8.03	25	8.13	8.00	8.03	0.99	12.4	9
	µg/l	TN3		1.15	33.6	15	36.5	32.8	33.6	2.3	6.8	10
	µg/l	V4M			0.72		0.54	0.72	0.76	0.19	24.7	7
Sr	µg/l	A1M		-0.73	110	10	106	106	106	5	5.1	9
	µg/l	P2M		0.33	200	15	205	200	199	16	7.9	8
	µg/l	TN3		0.18	150	15	152	150	148	9	6.3	10
	µg/l	V4M		0.00	79.2	10	79.2	79.2	80.7	3.7	4.5	9
Ti	µg/l	A1M		-0.23	35.5	10	35.1	35.4	35.2	1.6	4.7	10
	µg/l	P2M		0.05	16.0	25	16.1	16.0	16.2	2.1	13.2	8
	µg/l	TN3		0.00	116	10	116	116	116	4	3.7	10
	µg/l	V4M		-0.24	50.1	10	49.5	50.1	49.9	1.8	3.7	10
V	µg/l	A1M		-0.30	13.5	10	13.3	13.1	13.3	0.8	5.9	10
	µg/l	P2M		0.10	6.19	20	6.25	6.19	6.35	0.54	8.6	10
	µg/l	TN3		0.10	132	15	133	132	132	4	3.3	9
	µg/l	V4M		0.12	34.6	15	34.9	34.6	34.3	2.0	5.9	10
Zn	µg/l	A1M		-0.59	54.5	10	52.9	53.9	54.7	4.9	9.0	20
	µg/l	P2M		-0.42	21.3	20	20.4	20.4	21.4	2.7	12.8	13
	µg/l	TN3		0.16	170	15	172	173	169	13	7.8	18
	µg/l	V4M		0.00	42.5	15	42.5	42.4	42.6	2.0	4.6	14

Participant 25												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Al	µg/l	A1M		7.79	115	15	182	112	112	12	10.9	13
	µg/l	TY3		0.26	96.0	25	99.1	96.0	94.4	14.4	15.3	7
Co	µg/l	A1M		-1.21	11.0	15	10.0	10.5	10.4	0.8	7.6	16
	µg/l	TY3		-0.65	10.7	20	10.0	10.7	11.0	1.0	9.3	6
Cr	µg/l	A1M		-2.67	15.0	15	12.0	14.5	14.7	1.4	9.5	18
	µg/l	TY3		-0.67	13.1	25	12.0	13.1	13.9	2.3	16.4	7
Fe	µg/l	A1M		0.26	230	10	233	223	223	13	5.8	21
	µg/l	TY3			154		194	154	158	11	6.7	5
Mg	mg/l	A1M		-1.19	13.5	10	12.7	13.2	13.2	0.4	3.3	17
	mg/l	TY3		-0.21	19.3	15	19.0	19.3	19.9	1.3	6.4	6
Zn	µg/l	A1M		3.12	54.5	10	63.0	53.9	54.7	4.9	9.0	20
	µg/l	TY3			171		18	171	167	24	14.6	5

APPENDIX 8: Summary of the z scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	25	%
Al	A1M	Q	.	.	S	q	S	u	.	.	.	U	S	S	U	S	.	S	S	S	u	S	.	S	U	58.8
	P2M	Q	.	.	.	S	S	S	.	.	.	.	S	.	.	S	.	.	S	S	q	S	.	S	.	81.8
	TN3	S	.	.	.	S	S	S	.	.	.	.	.	U	U	S	.	S	S	S	S	S	.	S	.	84.6
	TY3	S	.	.	S	.	S	.	.	.	.	S	S	.	.	S	.	.	.	.	.	.	.	.	S	100
	V4M	S	.	.	.	S	S	q	.	.	.	.	S	.	.	S	.	S	S	S	u	S	.	S	.	83.3
As	A1M	S	.	.	.	S	S	S	.	S	.	.	S	S	.	S	.	S	q	S	.	S	.	S	.	92.3
	P2M	S	.	.	.	u	S	S	.	Q	.	.	S	.	.	S	.	.	S	S	.	S	.	S	.	81.8
	TN3	S	.	.	.	S	S	S	S	S	.	.	.	S	U	S	.	S	S	S	.	S	.	S	.	92.9
	V4M	S	.	.	.	u	S	S	.	U	S	.	S	.	.	S	.	.	S	S	.	S	.	S	.	83.3
B	A1M	Q	.	.	.	q	.	S	.	.	.	.	q	.	.	S	.	S	U	S	u	q	.	S	.	45.5
	P2M	Q	.	.	.	q	.	S	.	.	.	.	S	.	.	S	.	.	U	S	S	S	.	S	.	70.0
	TN3	S	.	.	.	S	Q	S	.	.	.	.	.	.	.	S	.	S	U	S	S	S	.	S	.	81.8
	V4M	S	.	.	.	S	.	S	.	.	.	.	S	.	.	S	.	S	U	S	S	S	.	S	.	90.9
Ba	A1M	S	.	.	.	S	S	u	.	.	.	.	q	S	.	S	.	.	S	S	.	S	.	S	.	81.8
	P2M	S	.	.	.	q	S	S	.	.	.	.	S	.	.	S	.	.	S	S	.	S	.	S	.	90.0
	TN3	Q	.	.	.	S	S	S	.	.	.	.	.	S	.	S	.	.	S	S	.	S	.	S	.	90.0
	V4M	S	.	.	.	S	S	S	.	.	.	.	S	.	.	S	.	.	S	S	.	S	.	S	.	100
Ca	A1M	S	.	S	.	S	S	Q	.	.	.	.	S	S	S	S	.	S	S	S	S	S	.	S	.	93.3
	P2M	S	.	.	.	S	S	S	.	.	.	.	S	.	.	S	.	.	S	S	S	S	.	S	.	100
	TN3	S	.	S	.	S	S	S	.	.	.	.	S	S	S	S	.	S	S	S	S	S	.	S	.	100
	V4M	S	.	.	.	S	S	S	.	.	.	.	S	.	.	S	.	S	S	S	S	S	.	S	.	100
Cd	A1M	S	.	.	.	S	S	S	.	S	.	.	S	S	.	S	.	S	S	S	.	S	.	S	.	100
	P2M	S	.	.	.	S	S	S	.	S	.	.	S	.	.	S	.	.	S	S	.	S	.	S	.	100
	TN3	S	S	.	.	S	S	S	.	S	.	.	.	S	.	S	.	S	S	S	.	S	.	S	.	100
	TY3	S	.	.	.	.	S	.	S	.	S	.	S	.	.	S	.	.	.	.	.	.	.	.	.	100
	V4M	S	.	.	.	S	S	S	.	S	.	.	S	.	.	S	.	S	S	S	.	S	.	S	.	100
Co	A1M	S	.	.	.	S	S	S	.	S	.	S	S	S	S	S	.	u	S	S	.	S	.	S	S	93.8
	P2M	Q	.	.	.	S	S	S	.	S	.	.	S	.	.	S	.	.	S	S	.	S	.	S	.	90.9
	TN3	Q	U	.	.	S	S	S	.	S	.	.	.	S	S	S	.	q	S	S	.	S	.	S	.	78.6
	TY3	S	.	.	.	.	S	.	.	.	.	S	S	.	.	S	.	.	.	.	.	.	.	.	S	100
	V4M	S	.	.	.	S	S	q	.	S	.	.	S	.	.	S	.	u	S	S	.	S	.	S	.	83.3
Cr	A1M	S	.	.	S	S	S	S	.	S	.	S	S	S	Q	S	S	S	S	S	.	S	.	S	q	88.9
	P2M	Q	.	.	.	S	S	S	.	S	.	.	S	.	.	S	.	.	S	S	.	S	.	S	.	90.9
	TN3	S	S	.	.	S	S	S	.	S	.	.	.	S	U	S	S	S	S	S	.	S	.	S	.	93.3
	TY3	Q	.	.	S	.	S	.	.	.	.	S	S	.	.	S	.	.	.	.	.	.	.	.	S	85.7
	V4M	S	.	.	.	S	S	S	.	S	.	.	S	.	.	S	.	S	S	S	.	S	.	S	.	100
Cu	A1M	S	S	S	S	S	S	S	.	S	.	.	u	S	S	S	.	S	S	S	S	q	.	S	.	88.9
	P2M	S	.	.	.	S	S	S	.	S	S	.	S	.	.	S	.	.	S	S	S	S	.	S	.	100
	TN3	S	.	S	.	S	S	S	.	S	.	.	.	S	S	S	.	S	S	S	S	S	.	S	.	100
	TY3	Q	.	.	S	.	S	.	.	.	S	.	S	.	.	S	.	.	.	.	.	.	.	.	.	83.3
	V4M	S	.	.	.	S	S	S	.	S	.	.	S	.	.	S	.	Q	S	S	S	S	.	S	.	92.3
Fe	A1M	S	S	q	S	S	S	u	.	S	q	q	S	S	S	S	S	S	S	S	S	S	.	S	S	81.8
	P2M	S	.	.	.	S	S	u	.	S	Q	.	S	.	.	S	.	.	S	S	S	S	.	S	.	84.6
	TN3	Q	S	S	.	S	S	S	u	S	.	.	S	S	S	S	S	S	S	S	S	S	.	S	.	89.5
	V4M	Q	.	.	.	S	S	S	.	S	.	.	S	.	.	S	.	S	S	S	U	S	.	S	.	84.6

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	25	%
Hg	A1Hg	S	.	.	S	S	S	.	.	S	U	.	q	S	.	S	.	.	Q	S	.	S	S	S	.	78.6
	P2Hg	U	.	.	.	S	Q	.	.	S	U	.	S	.	.	S	.	.	S	S	.	S	S	S	.	75.0
	T3Hg	S	.	.	S	S	S	.	.	S	S	.	q	S	.	S	.	.	S	S	.	S	S	S	.	92.9
	V4Hg	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
K	A1M	S	.	.	.	S	S	S	.	.	.	.	S	.	.	S	.	S	S	S	S	S	.	S	.	100
	P2M	U	.	.	.	S	S	S	.	.	.	.	S	.	.	S	.	.	S	S	S	S	.	S	.	90.9
	TN3	Q	.	.	.	S	S	S	.	.	.	.	.	.	.	S	.	S	S	S	S	S	.	S	.	90.9
	V4M	S	.	.	.	S	S	S	.	.	.	.	S	.	.	S	.	S	S	S	S	S	.	S	.	100
Mg	A1M	S	S	.	.	S	S	S	.	.	.	S	S	S	S	S	.	S	S	S	S	S	.	S	S	100
	P2M	Q	.	.	.	S	S	S	.	.	.	.	S	.	.	S	.	.	S	S	S	S	.	S	.	90.9
	TN3	S	S	.	.	S	S	S	.	.	.	.	.	S	S	S	.	S	S	S	S	S	.	S	.	100
	TY3	Q	.	.	.	.	S	.	.	.	.	S	S	.	.	S	.	.	.	.	.	.	.	.	S	83.3
	V4M	S	.	.	.	S	S	S	.	.	.	.	S	.	.	S	.	S	S	S	S	S	.	S	.	100
Mn	A1M	S	S	S	S	S	S	u	.	.	.	.	S	S	S	S	.	S	S	S	S	q	.	S	.	88.2
	P2M	S	.	.	.	S	S	S	.	.	.	.	S	.	.	S	.	.	S	S	S	S	.	S	.	100
	TN3	S	S	S	.	S	S	S	.	.	.	.	S	S	S	S	.	S	S	S	S	S	.	S	.	100
	V4M	S	.	.	.	S	S	S	.	.	.	.	S	.	.	S	.	S	S	S	S	S	.	S	.	100
Mo	A1M	U	S	.	.	S	S	S	.	S	.	.	q	S	.	S	S	.	S	S	S	S	.	S	.	86.7
	P2M	U	.	.	.	q	S	S	.	S	.	.	S	.	.	S	.	.	S	S	S	S	.	S	.	83.3
	TN3	u	S	.	.	S	Q	S	.	q	.	.	S	S	.	S	S	.	S	S	q	S	.	S	.	73.3
	V4M	U	.	.	.	S	S	S	.	S	.	.	q	.	.	S	.	.	S	S	U	S	.	S	.	75.0
Ni	A1M	S	.	.	S	S	S	S	.	S	.	.	u	S	U	q	S	S	S	S	.	S	.	S	.	81.3
	P2M	Q	.	.	.	S	S	S	.	S	.	.	S	.	.	S	.	.	S	S	.	S	.	S	.	90.9
	TN3	S	.	.	.	S	S	S	.	S	.	.	S	S	S	S	S	S	S	S	.	S	.	S	.	100
	V4M	S	.	.	.	S	S	S	.	S	.	.	S	.	.	S	.	Q	S	S	.	S	.	S	.	91.7
Pb	A1M	S	.	.	S	S	S	u	.	S	.	.	u	u	.	S	.	.	S	S	.	q	.	S	.	69.2
	P2M	S	.	.	.	S	S	u	.	u	.	.	q	.	.	q	.	.	S	S	.	S	.	S	.	63.6
	TN3	S	.	.	.	S	S	u	.	q	.	.	.	S	.	S	.	u	S	S	.	S	.	S	.	75.0
	TY3	S	.	.	S	.	S	.	.	.	S	.	S	.	.	S	.	.	.	.	.	.	.	.	.	100
	V4M	S	.	.	.	U	S	u	.	q	S	.	S	.	.	S	.	.	S	S	.	q	.	S	.	66.7
Sb	A1M	q	.	.	.	S	S	S	.	S	.	.	u	S	.	S	.	.	S	S	.	S	.	S	.	83.3
	P2M	S	.	.	.	S	S	S	.	S	.	.	S	.	.	S	.	.	S	S	.	S	.	S	.	100
	TN3	S	.	.	.	S	S	S	.	S	.	.	.	S	S	S	.	.	S	S	.	S	.	S	.	100
	V4M	S	.	.	.	S	S	S	.	q	.	.	S	.	.	S	.	.	S	S	.	S	.	S	.	90.9
Se	A1M	Q	.	.	.	S	S	u	.	S	.	.	S	S	.	S	.	.	S	S	.	S	.	S	.	83.3
	P2M	S	.	.	.	S	S	S	.	S	.	.	S	.	.	S	.	.	S	S	.	S	.	S	.	100
	TN3	S	.	.	.	S	S	S	.	S	.	.	.	S	.	S	.	.	S	S	.	S	.	S	.	100
	V4M	S	.	.	.	S	S	q	.	S	.	.	S	.	.	S	.	.	S	S	.	S	.	S	.	90.9
Sn	A1M	S	.	.	.	S	S	q	.	.	.	.	S	S	.	S	.	.	S	S	.	S	.	S	.	90.9
	P2M	S	.	.	.	S	S	S	.	.	.	.	U	.	.	S	.	.	S	S	.	S	.	S	.	90.0
	TN3	S	.	.	.	S	S	S	.	.	.	.	.	S	.	S	.	.	S	S	.	S	.	S	.	100
	V4M	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
Sr	A1M	u	.	.	.	S	S	q	.	.	.	.	S	U	.	S	.	S	S	S	.	.	.	S	.	72.7
	P2M	S	.	.	.	S	S	S	.	.	.	.	S	.	.	S	.	.	S	Q	.	.	.	S	.	88.9
	TN3	S	.	.	.	S	S	S	.	.	.	.	.	S	.	S	.	S	S	S	.	.	.	S	.	100
	V4M	S	.	.	.	S	S	S	.	.	.	.	S	.	.	S	.	S	S	Q	.	.	.	S	.	90.0

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	25	%
Ti	A1M	*S*	.	.	.	*S*	*S*	*S*	.	.	.	.	**S**	.	.	**S**	.	.	*S*	**S**	.	*S*	.	*S*	.	100
	P2M	*S*	.	.	.	*S*	*Q*	*S*	.	.	.	.	**S**	.	.	**S**	.	.	*S*	.	.	*S*	.	*S*	.	88.9
	TN3	*S*	.	.	.	*S*	*S*	*S*	.	.	.	.	**S**	.	.	**S**	.	.	*S*	**S**	.	*S*	.	*S*	.	100
	V4M	*S*	.	.	.	*S*	*S*	*S*	.	.	.	.	**S**	.	.	**S**	.	.	*S*	**S**	.	*S*	.	*S*	.	100
V	A1M	**Q**	.	.	.	*S*	*S*	*S*	.	.	.	.	**S**	.	.	**S**	.	.	**S**	**S**	.	**S**	.	**S**	.	90.0
	P2M	**Q**	.	.	.	*S*	*S*	*S*	.	.	.	.	**S**	.	.	**S**	.	.	**S**	**S**	.	**S**	.	**S**	.	90.0
	TN3	**Q**	.	.	.	*S*	*S*	*S*	.	.	.	.	**S**	.	.	**S**	.	.	**S**	**S**	.	**S**	.	**S**	.	90.0
	V4M	**S**	.	.	.	*S*	*S*	*S*	.	.	.	.	**S**	.	.	**S**	.	.	**S**	**S**	.	**S**	.	**S**	.	100
Zn	A1M	**Q**	*U*	*S*	*Q*	*S*	*S*	*S*	.	*S*	.	**u**	**S**	*S*	*u*	**S**	*S*	*S*	**S**	**S**	**S**	**S**	.	**S**	*U*	71.4
	P2M	**S**	.	.	.	*S*	*S*	*S*	.	*S*	**S**	.	**Q**	.	.	**S**	.	.	**S**	**S**	*S*	**S**	.	**S**	.	92.3
	TN3	**S**	*S*	*S*	.	*S*	*q*	*u*	*S*	*S*	.	.	**S**	*S*	*S*	**S**	*S*	*S*	**S**	**S**	*S*	**S**	.	**S**	.	89.5
	V4M	**S**	.	.	.	*S*	*S*	*S*	.	*S*	**S**	.	**S**	.	.	**S**	.	*S*	**S**	**S**	*S*	**S**	.	**S**	.	100
%		71	86	90	93	91	95	81	75	86	69	70	85	93	68	98	100	87	94	98	83	94	100	100	70	
akkreditoitu		86					57				11	10	84			97			86	93	10	66	3	81		

S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, italics - non-accredited, normal - unknown
% - percentage of satisfactory results

Totally satisfactory, % in all: 89 % in accredited: 91 % in non-accredited: 88

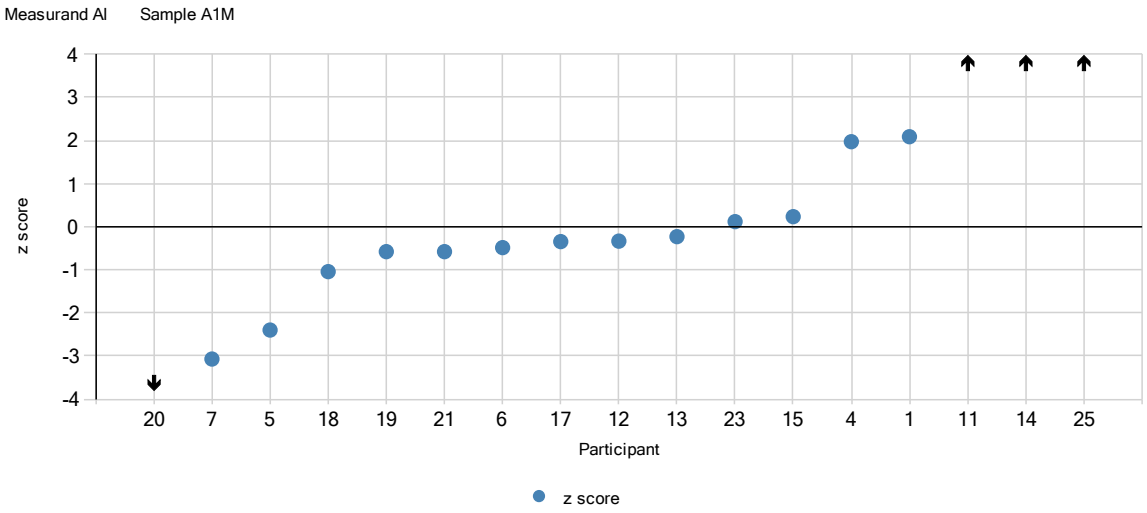
APPENDIX 9: Summary of the E_n scores

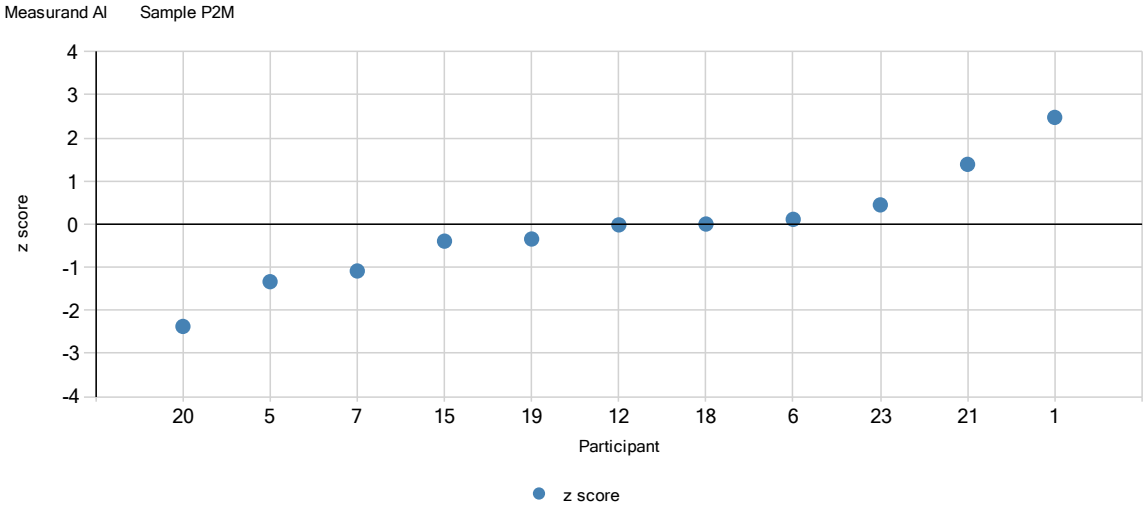
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
As	TY3	0.6	.	.	.	.	-0.5	.	.	.	-0.3	.	0.1	.	.	0.0	.	.	.	.	.	.	.	.	100
B	TY3	-0.3	.	.	.	.	.	.	.	.	.	.	0.0	.	.	0.0	.	.	.	.	.	.	.	.	100
Ba	TY3	0.5	.	.	.	.	0.1	.	.	.	.	.	-0.4	.	.	-0.1	.	.	.	.	.	.	.	.	100
Ca	TY3	0.4	.	.	.	.	0.0	.	.	.	.	.	.	.	.	-0.2	.	.	.	.	.	.	.	.	100
Cd	TY3	0.1	.	.	.	.	-0.1	.	.	.	-0.1	.	0.7	.	.	0.1	.	.	.	.	.	.	.	.	100
Co	TY3	0.9	.	.	.	.	-0.2	.	.	.	.	0.5	-0.1	.	.	0.1	.	.	.	.	.	.	.	.	100
Cr	TY3	1.6	.	.	-0.3	.	0.0	.	.	.	.	1.0	-0.4	.	.	0.4	.	.	.	.	.	.	.	.	83.3
Cu	TY3	1.2	.	.	0.3	.	0.0	.	.	.	-0.6	.	0.0	.	.	-0.2	.	.	.	.	.	.	.	.	83.3
Fe	TY3	0.8	.	.	0.2	.	0.0	.	.	.	.	-0.1	.	.	.	-0.1	.	.	.	.	.	.	.	.	100
Hg	V4Hg	1.1	.	.	.	.	0.1	.	.	.	-1.8	.	-2.4	.	.	0.3	.	.	1,3	-1,9	.	-0,2	-1,8	0,0	40.0
K	TY3	0.4	.	.	.	.	-0.1	.	.	.	.	.	0.0	.	.	0.0	.	.	.	.	.	.	.	.	100
Mg	TY3	1.2	.	.	.	.	-0.1	.	.	.	.	0.0	0.3	.	.	0.0	.	.	.	.	.	.	.	.	80.0
Mn	TY3	0.6	.	.	0.1	.	-0.1	.	.	.	.	.	.	.	.	-0.1	.	.	.	.	.	.	.	.	100
Mo	TY3	-7.0	.	.	.	.	0.3	.	.	.	.	.	.	.	.	-0.3	.	.	.	.	.	.	.	.	66.7
Ni	TY3	1.2	.	.	0.0	.	-0.4	.	.	.	.	.	.	.	.	-0.1	.	.	.	.	.	.	.	.	75.0
Se	TY3	0.3	.	.	.	.	-0.9	.	.	.	.	.	0.2	.	.	-0.3	.	.	.	.	.	.	.	.	100
Sn	TY3	0.1	.	.	.	.	-0.4	.	.	.	.	.	-0.1	.	.	0.3	.	.	.	.	.	.	.	.	100
Sr	TY3	0.6	.	.	.	.	0.0	.	.	.	.	.	0.0	.	.	0.0	.	.	.	.	.	.	.	.	100
Ti	TY3	0.1	.	.	.	.	.	.	.	.	.	.	.	.	.	-0.6	.	.	.	.	.	.	.	.	100
V	TY3	0.7	.	.	.	.	-0.3	.	.	.	.	.	.	.	.	0.0	.	.	.	.	.	.	.	.	100
Zn	TY3	0.8	.	.	0.0	.	-0.7	.	.	.	0.0	-7.2	.	.	.	-0.6	.	.	.	.	.	.	.	.	83.3
%		71			100		100				80	60	92			100						100		100	

E_n scores enable to estimate the proximity of participant results to the assigned value taking into consideration their reported expanded uncertainty
Scores of $-1.0 < E_n < 1.0$ indicate successful performance
Scores of $E_n \geq 1.0$ or $E_n \leq -1.0$ indicate a need to review the uncertainty estimated or to correct a measurement issue

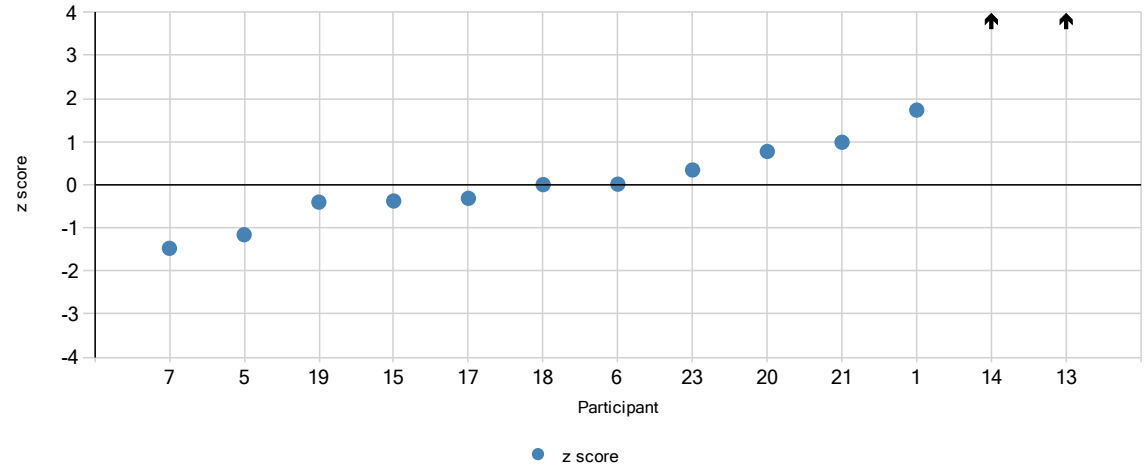
Totally satisfactory, % in all: 91

APPENDIX 10: z scores in ascending order

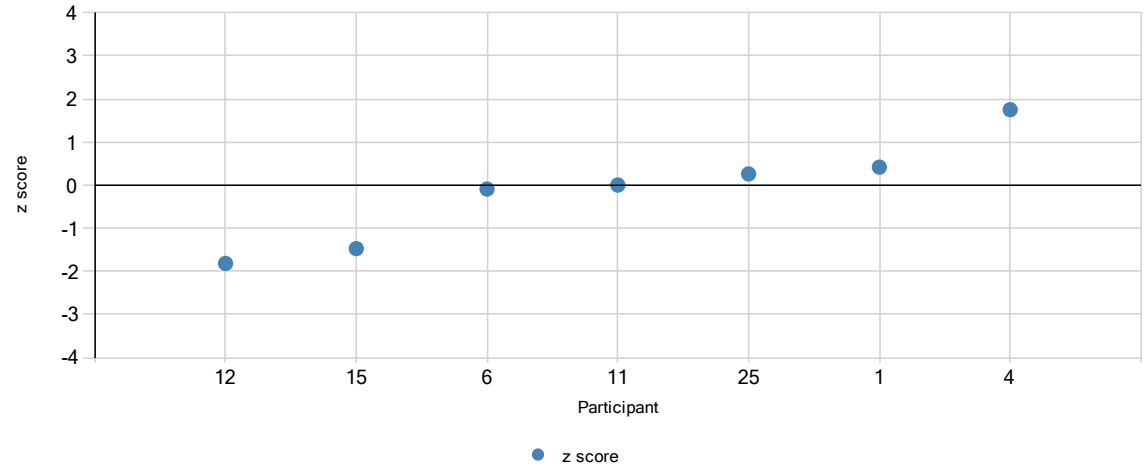




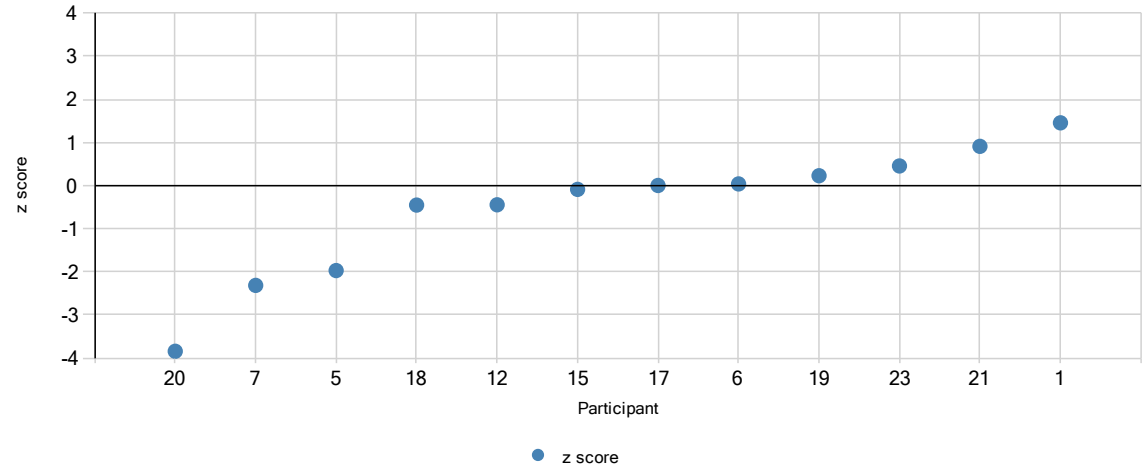
Measurand Al Sample TN3

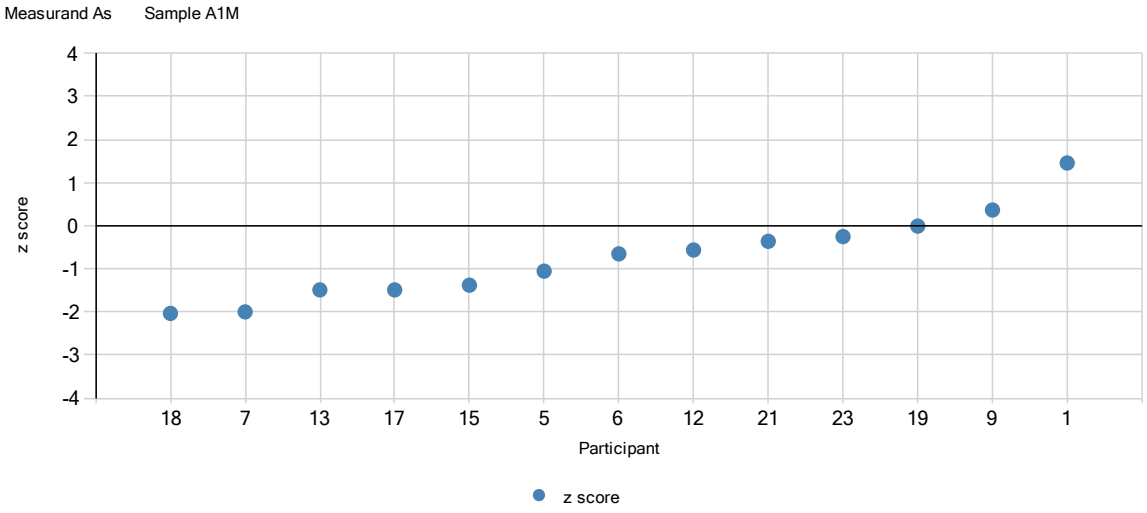


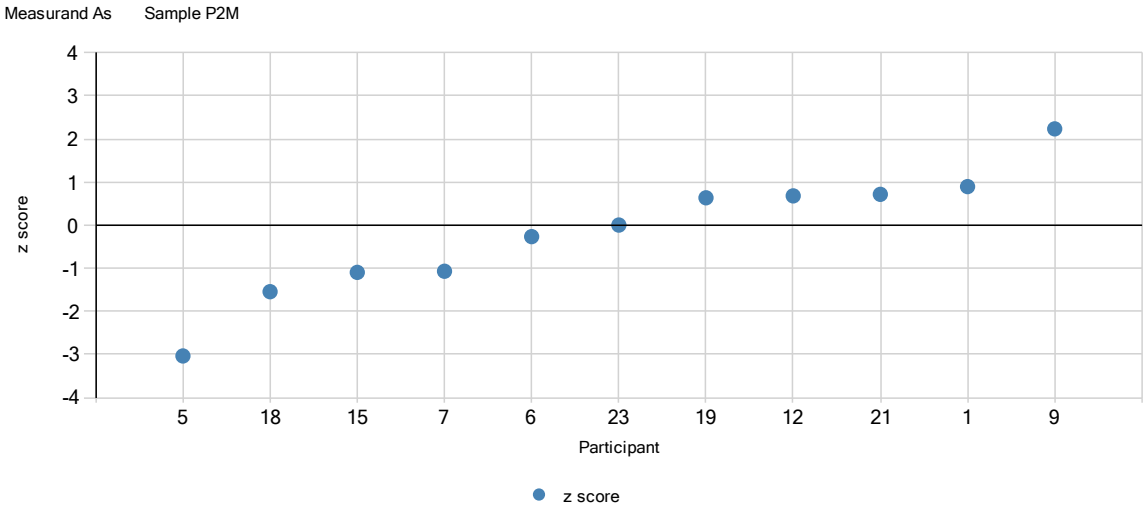
Measurand Al Sample TY3

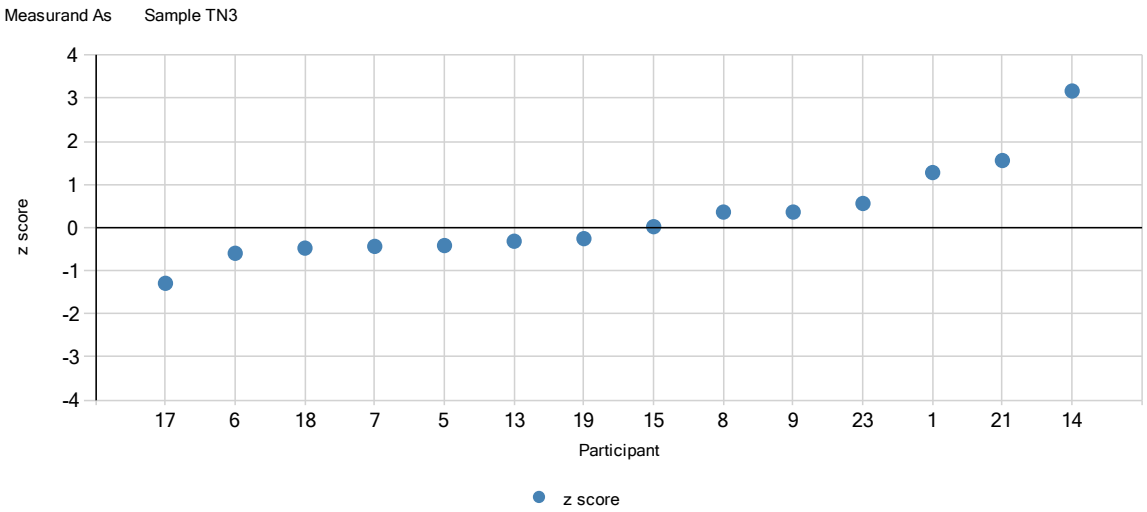


Measurand Al Sample V4M

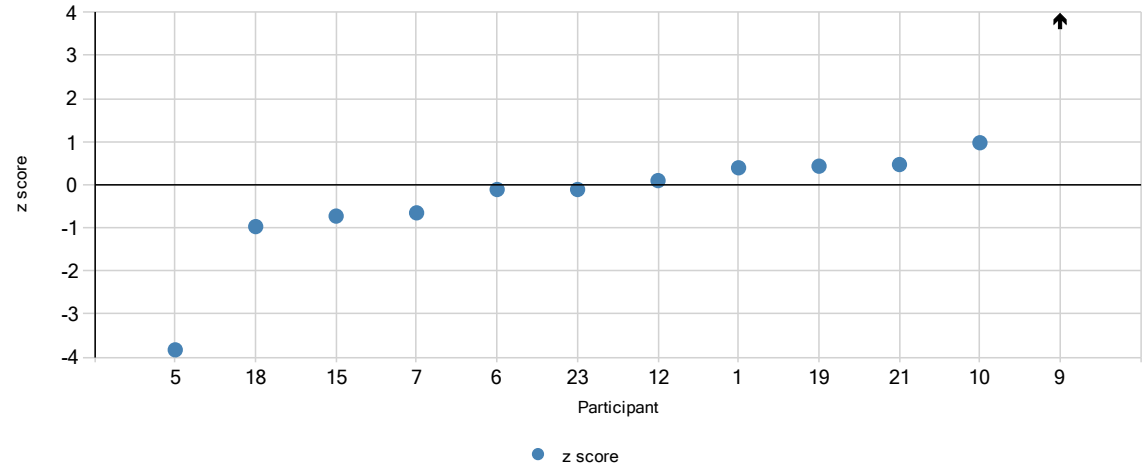



Measurand As Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
18 7 13 17 15 5 6 12 21 23 19 9 1
Participant
z score

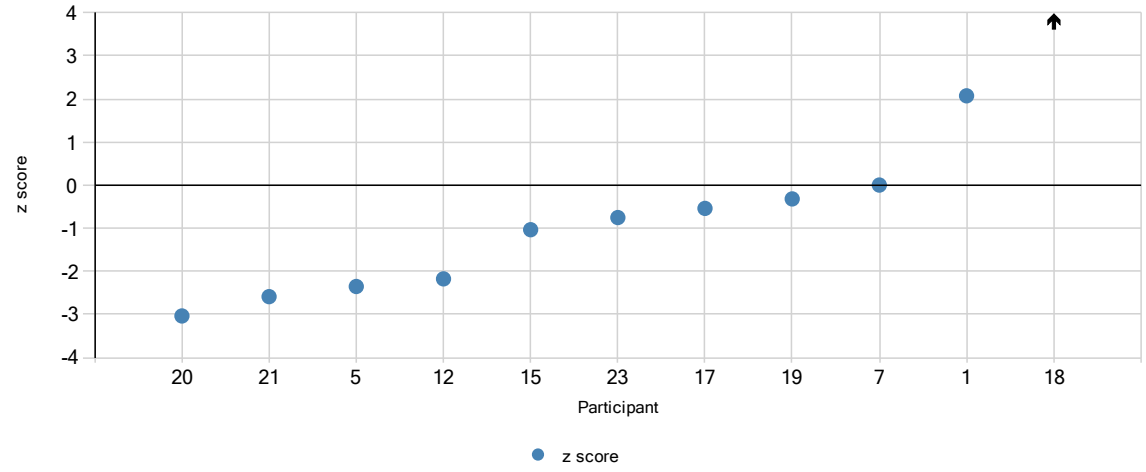

Measurand As Sample P2M
z score
4
3
2
1
0
-1
-2
-3
-4
5 18 15 7 6 23 19 12 21 1 9
Participant
z score


Measurand As Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
17 6 18 7 5 13 19 15 8 9 23 1 21 14
Participant
z score

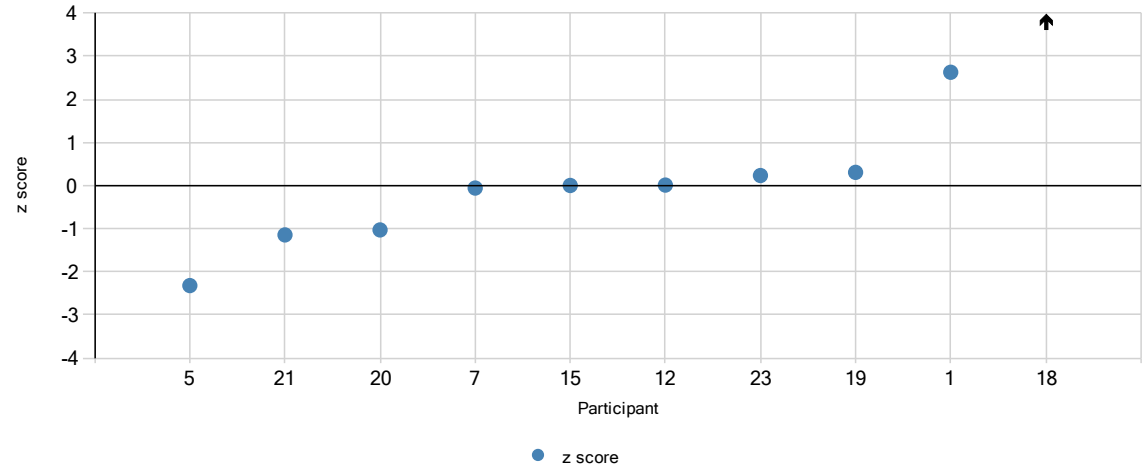
Measurand As Sample V4M

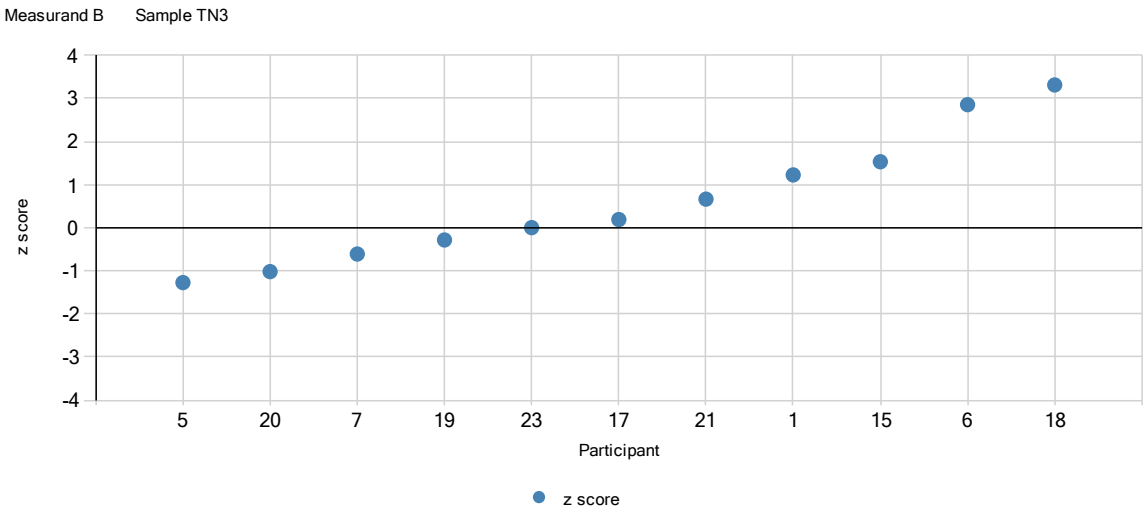


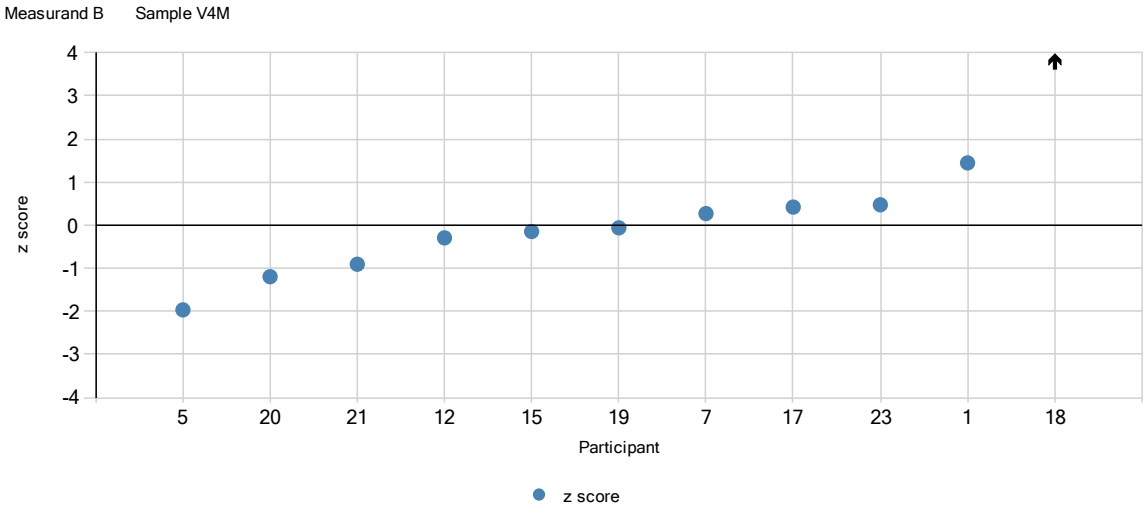
Measurand B Sample A1M

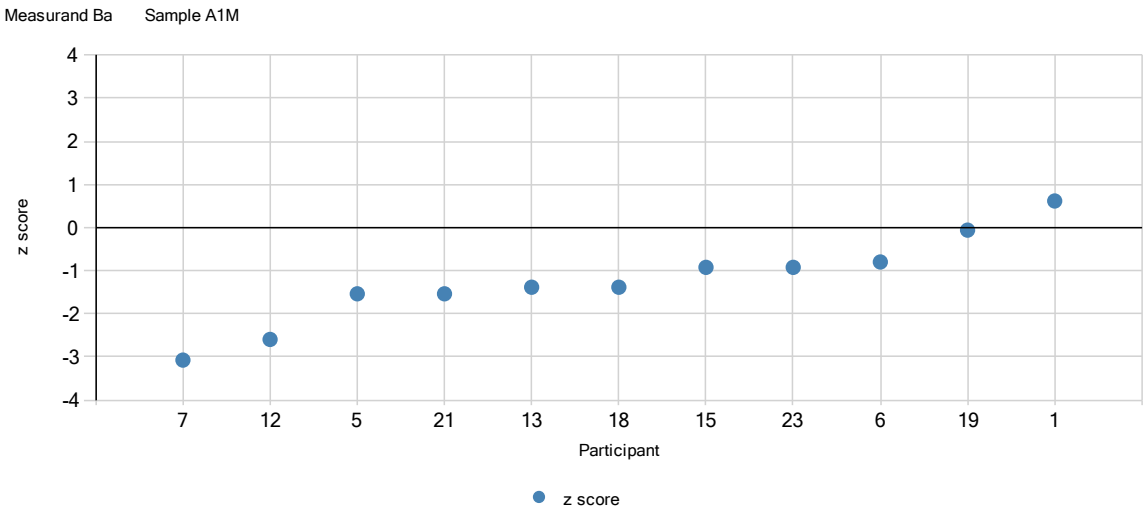


Measurand B Sample P2M




Measurand B Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
5 20 7 19 23 17 21 1 15 6 18
Participant
z score


Measurand B Sample V4M
z score
4
3
2
1
0
-1
-2
-3
-4
5 20 21 12 15 19 7 17 23 1 18
Participant
z score


Measurand Ba Sample A1M
z score
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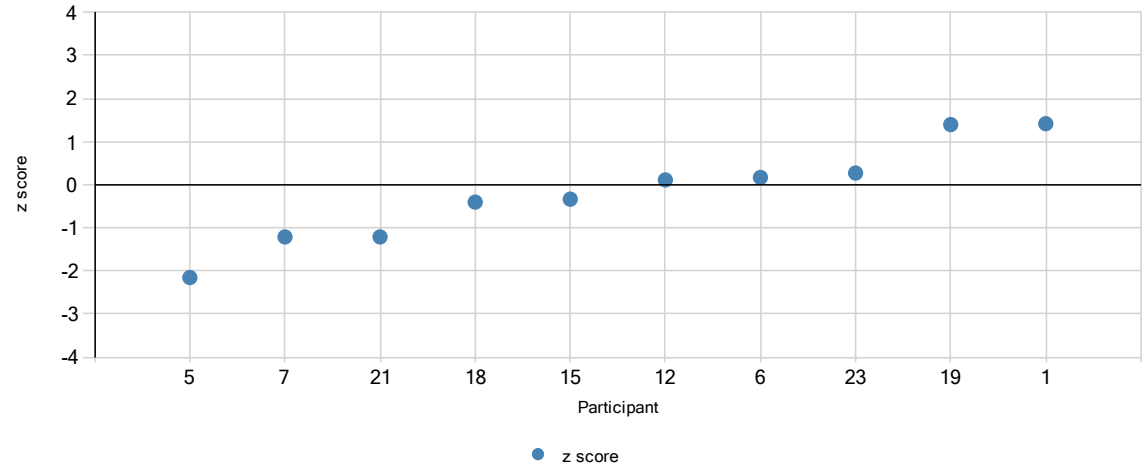
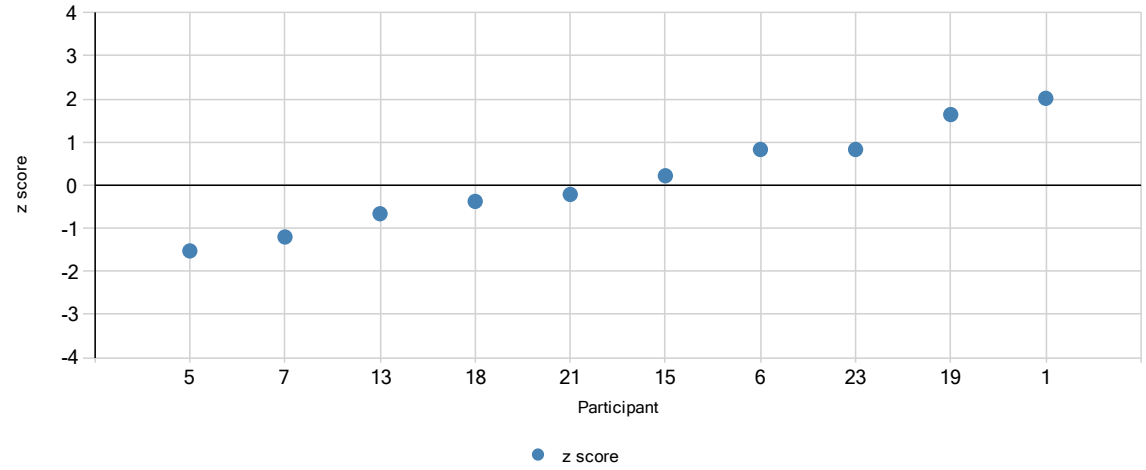
3
2
1
0
-1
-2
-3
-4
7 12 5 21 13 18 15 23 6 19 1
Participant
z score

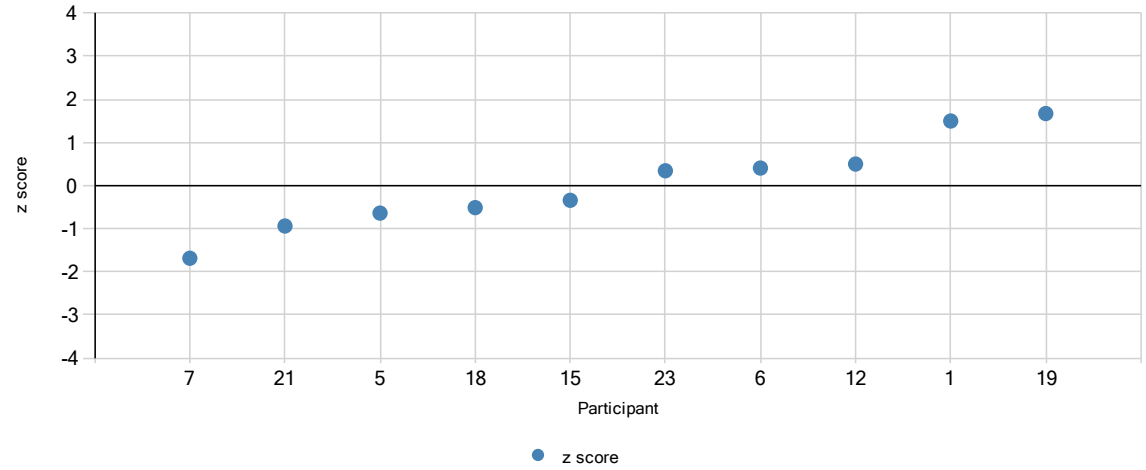
Measurand Ba Sample P2M

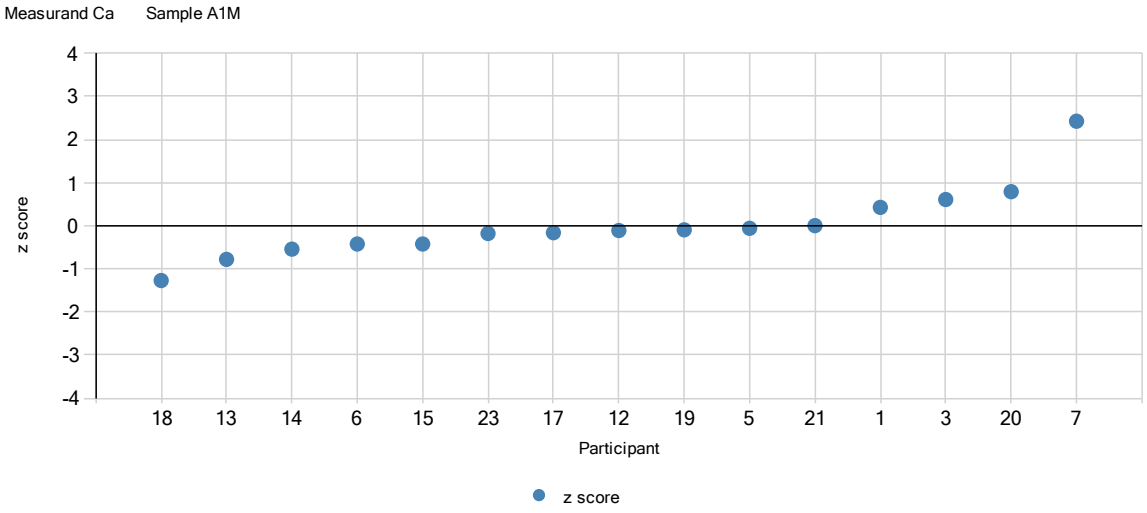


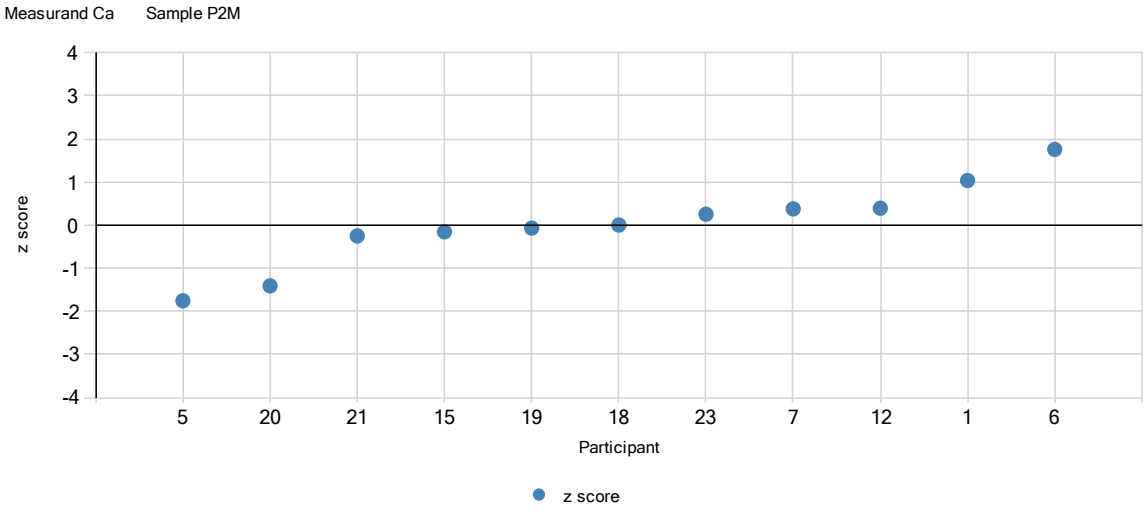
Measurand Ba Sample TN3



Measurand Ba Sample V4M




Measurand Ca Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
18 13 14 6 15 23 17 12 19 5 21 1 3 20 7
Participant
z score


Measurand Ca Sample P2M
z score
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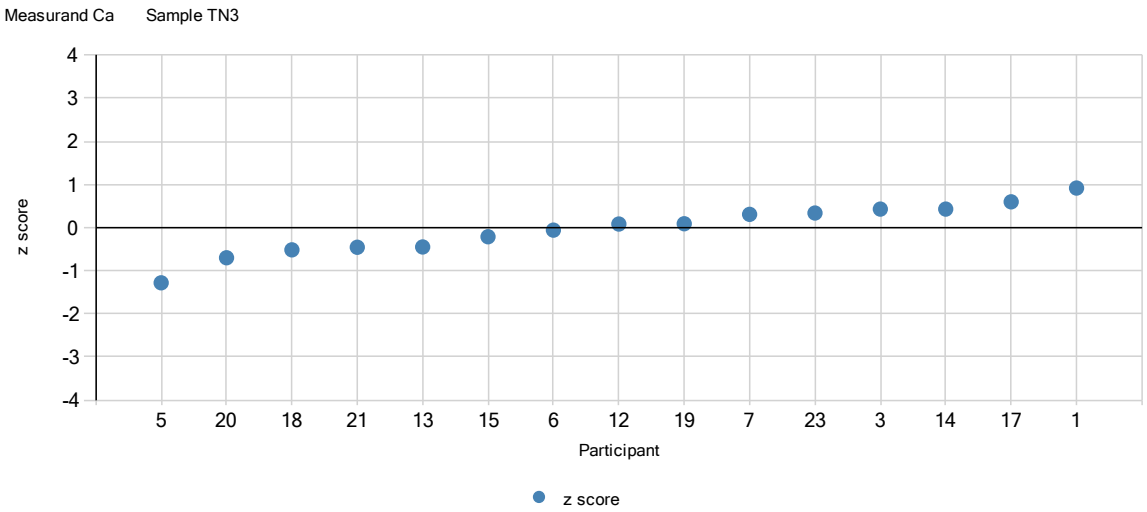
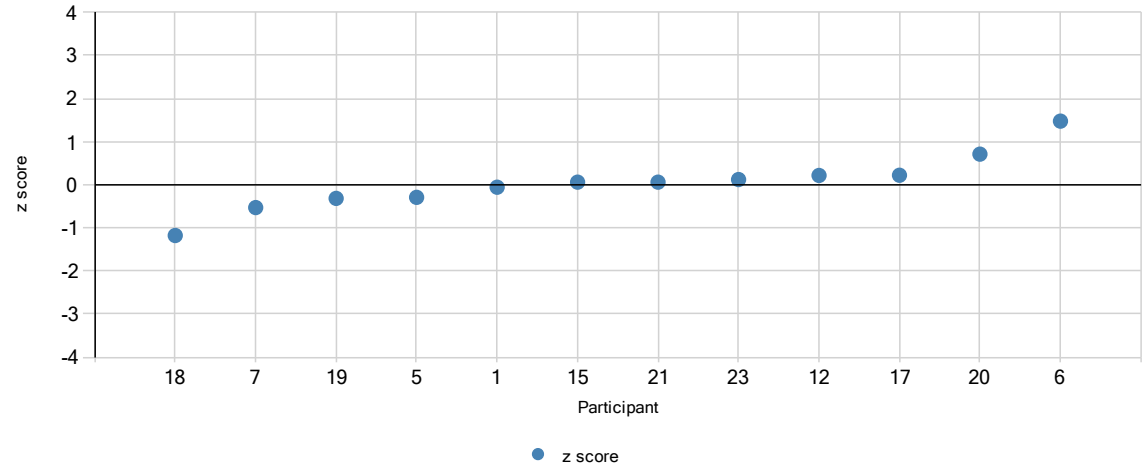
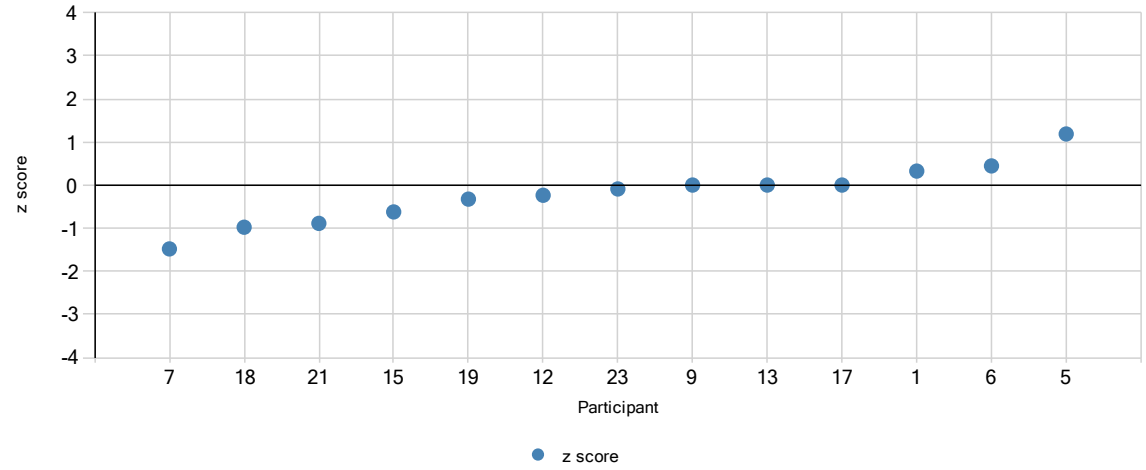
3
2
1
0
-1
-2
-3
-4
5 20 21 15 19 18 23 7 12 1 6
Participant
z score


Measurand Ca Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
5 20 18 21 13 15 6 12 19 7 23 3 14 17 1
Participant
z score

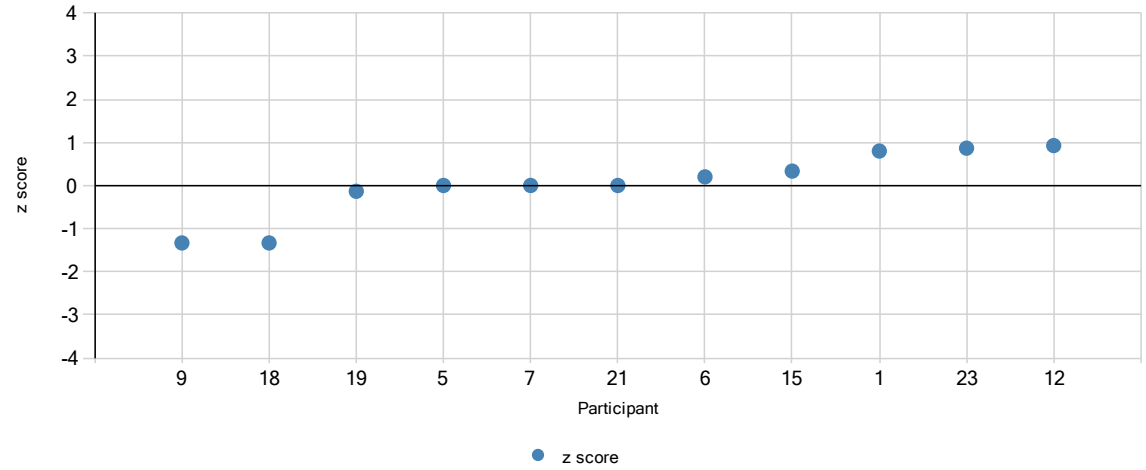
Measurand Ca Sample V4M

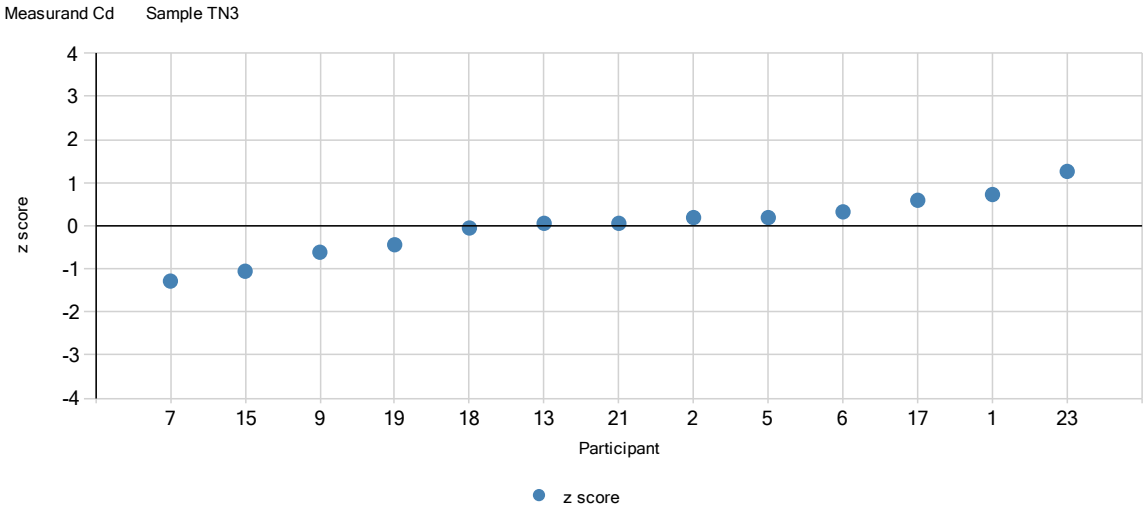


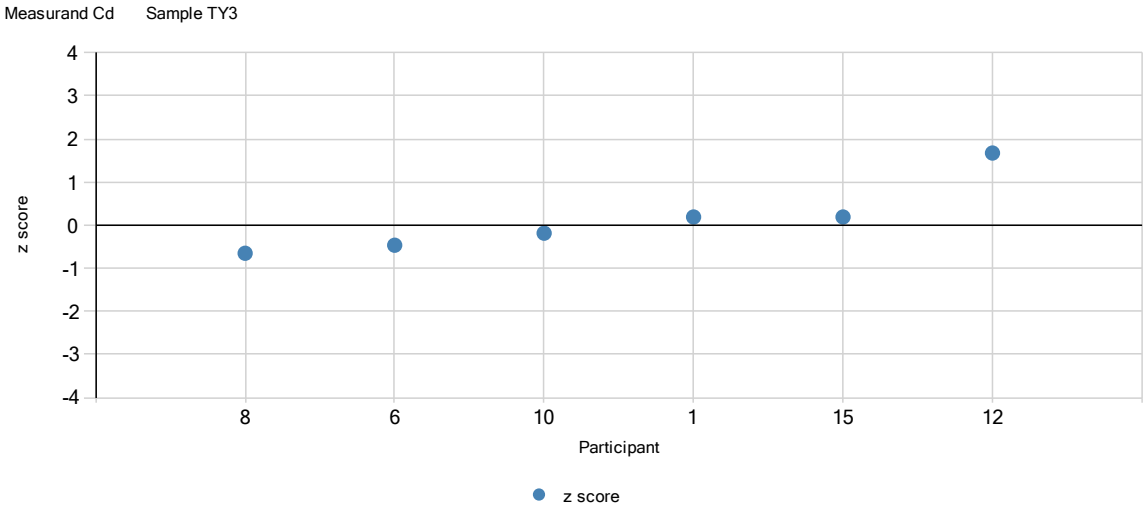
Measurand Cd Sample A1M

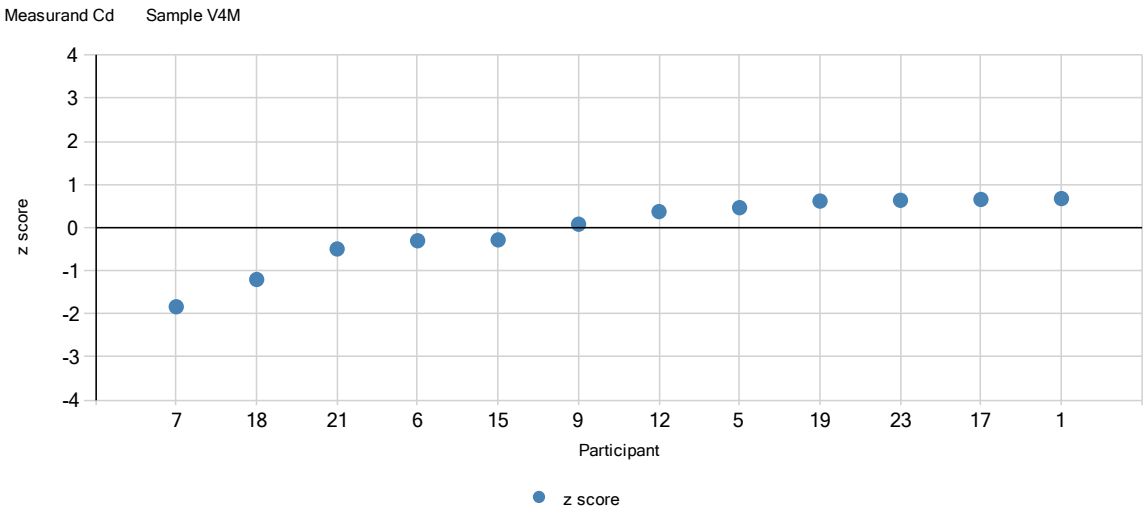


Measurand Cd Sample P2M

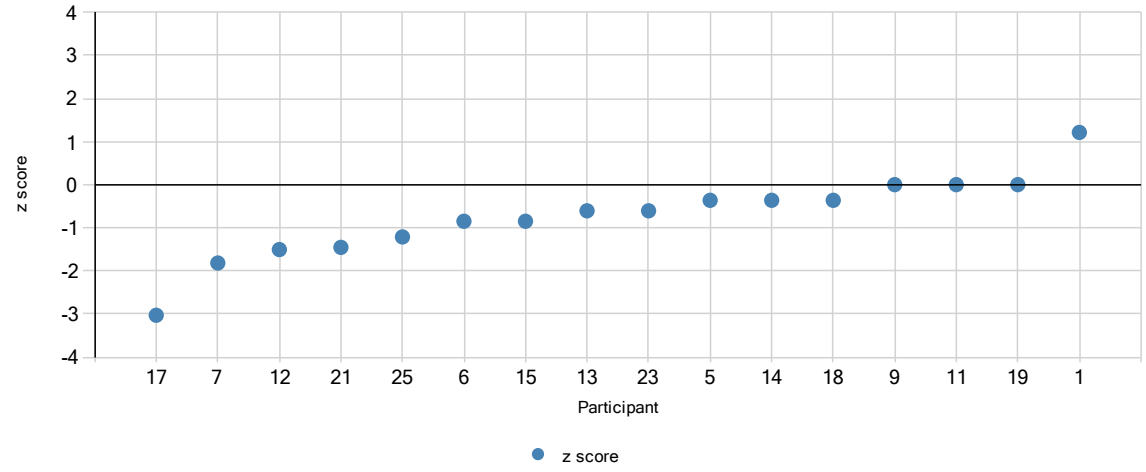



Measurand Cd Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
7 15 9 19 18 13 21 2 5 6 17 1 23
Participant
z score

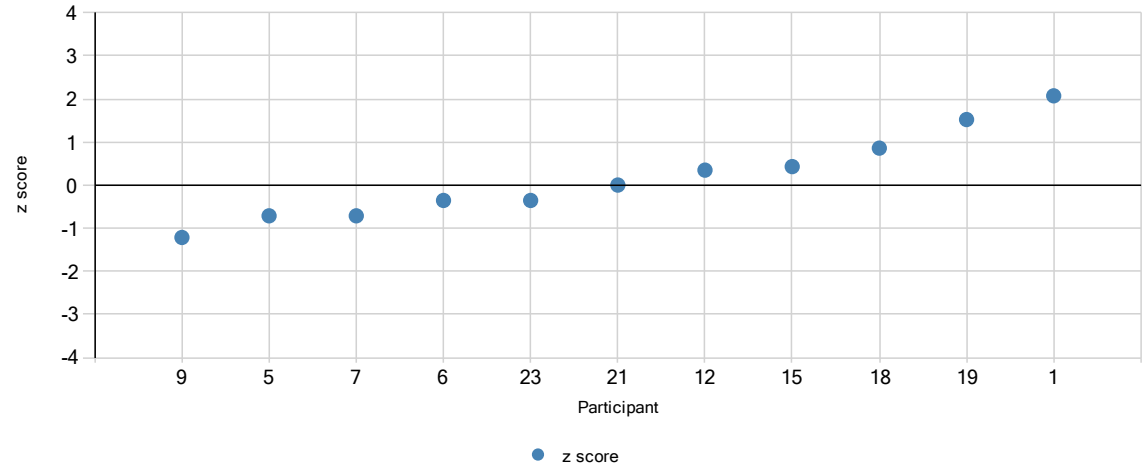

Measurand Cd Sample TY3
z score
4
3
2
1
0
-1
-2
-3
-4
8 6 10 1 15 12
Participant
z score


Measurand Cd Sample V4M
z score
4
3
2
1
0
-1
-2
-3
-4
7 18 21 6 15 9 12 5 19 23 17 1
Participant
z score

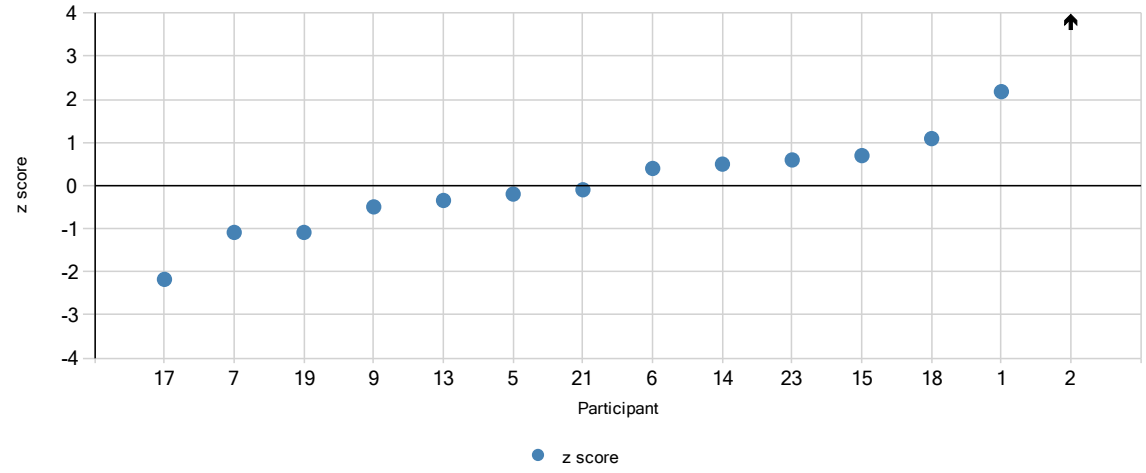
Measurand Co Sample A1M

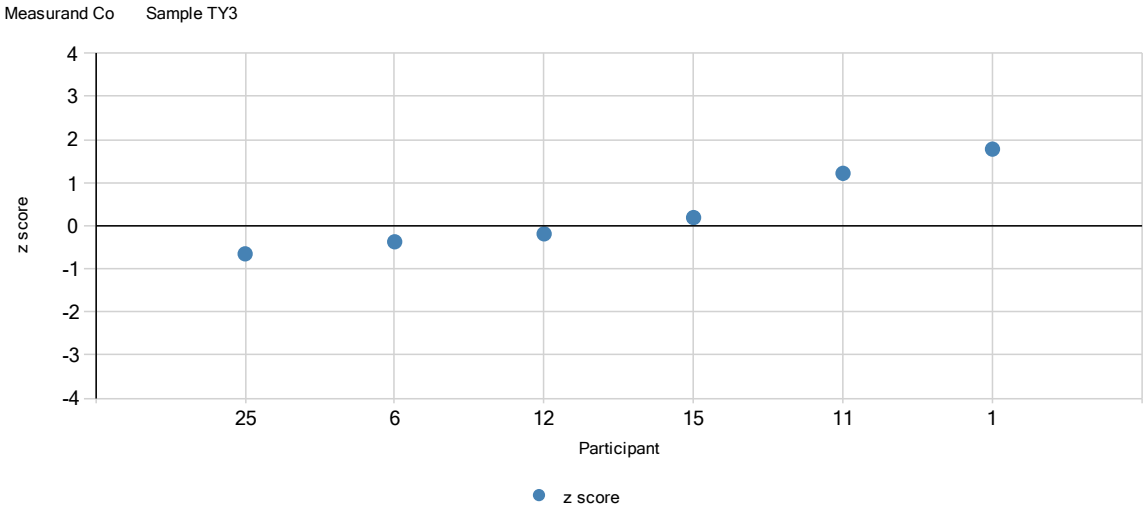


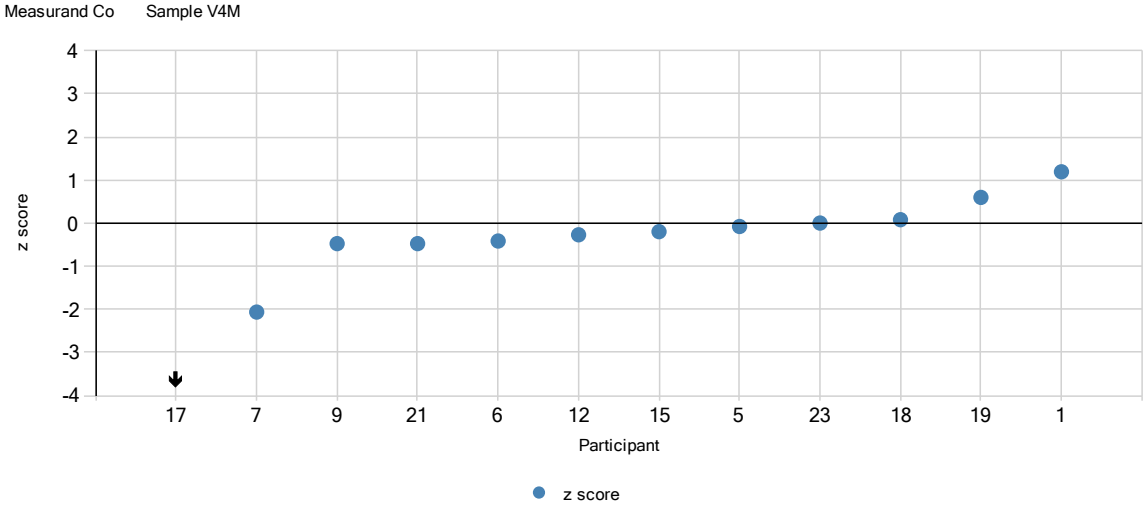
Measurand Co Sample P2M

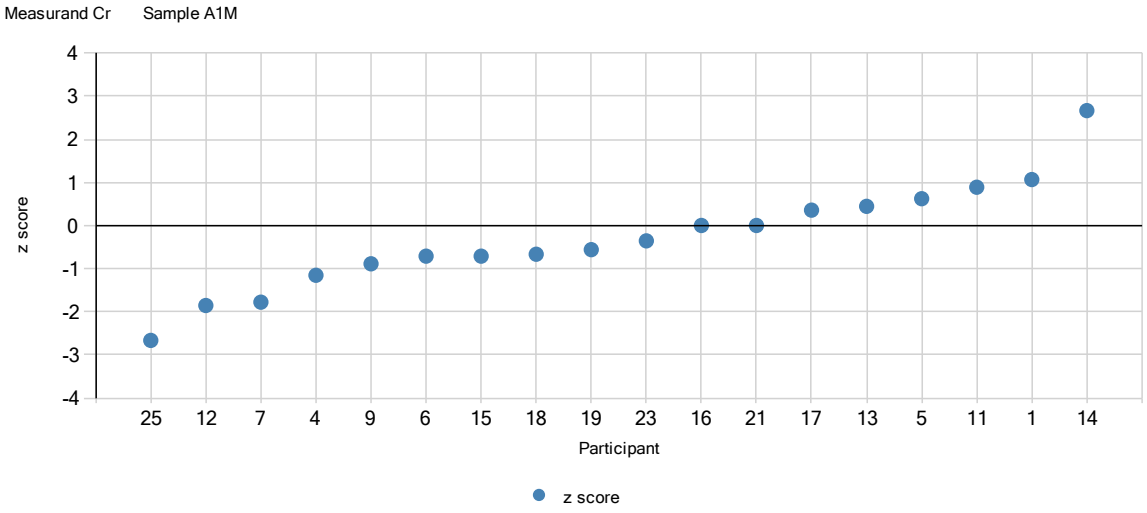


Measurand Co Sample TN3

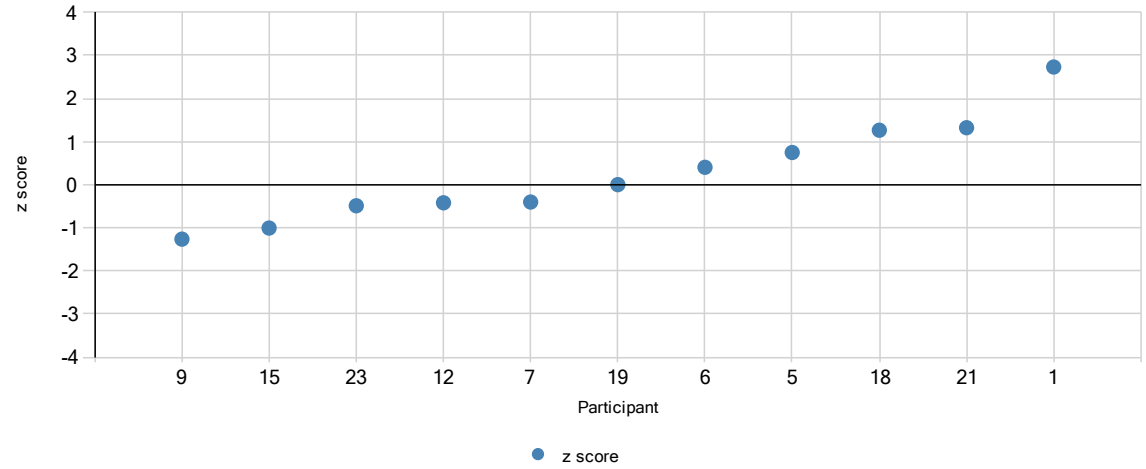



Measurand Co Sample TY3
z score
4
3
2
1
0
-1
-2
-3
-4
25
6
12
15
11
1
Participant
z score

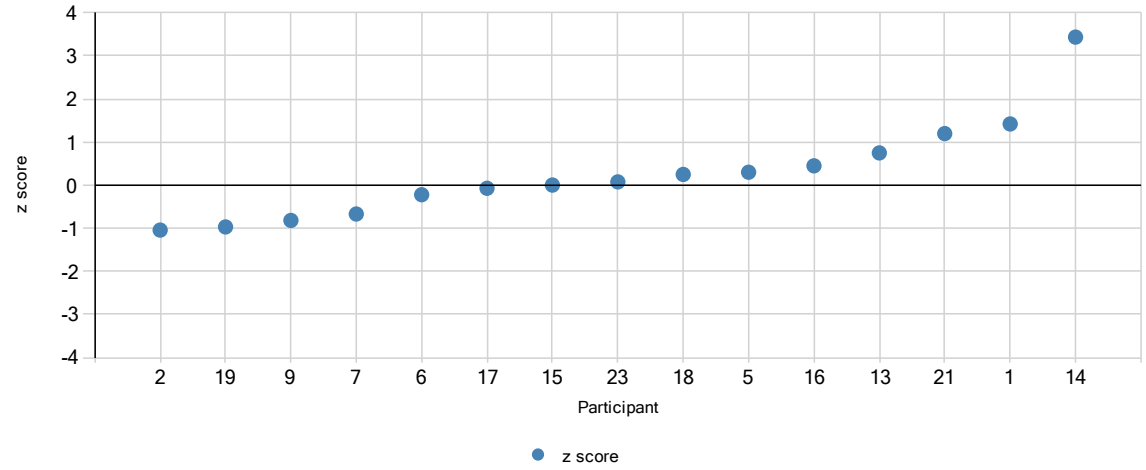

Measurand Co Sample V4M
z score
4
3
2
1
0
-1
-2
-3
-4
17
7
9
21
6
12
15
5
23
18
19
1
Participant
z score


Measurand Cr Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
25
12
7
4
9
6
15
18
19
23
16
21
17
13
5
11
1
14
Participant
z score

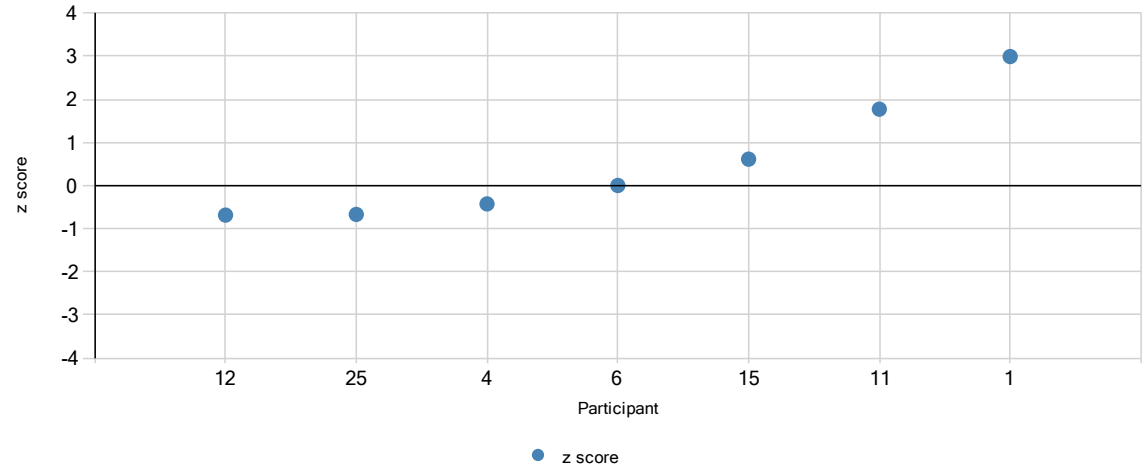
Measurand Cr Sample P2M



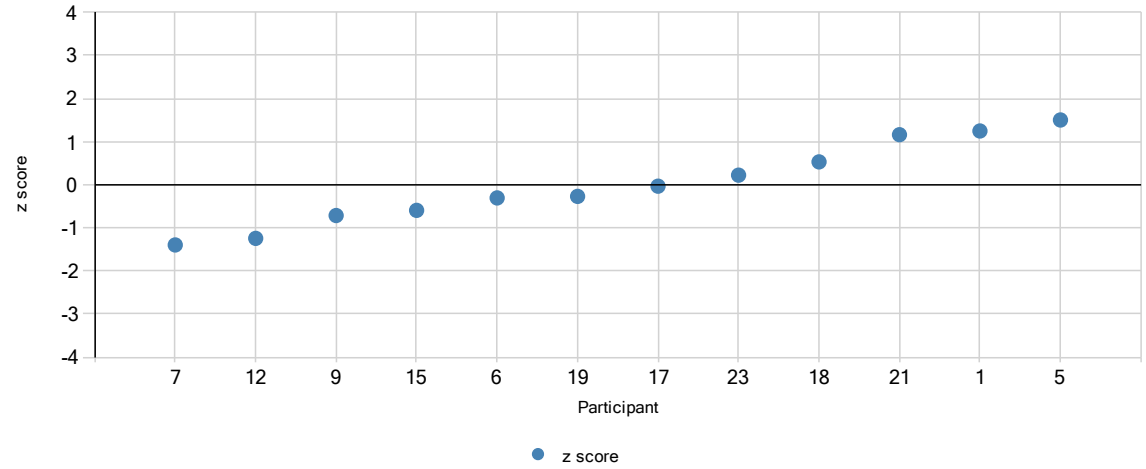
Measurand Cr Sample TN3



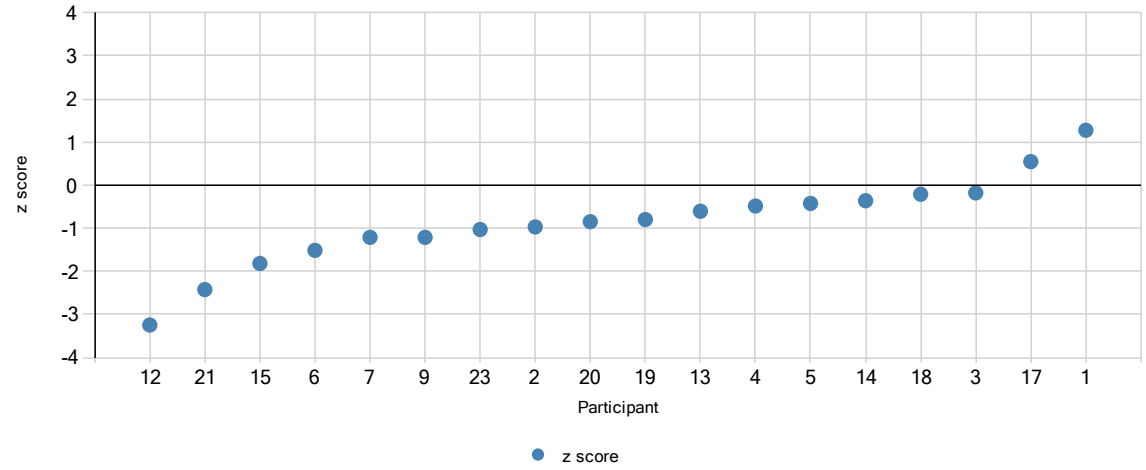
Measurand Cr Sample TY3



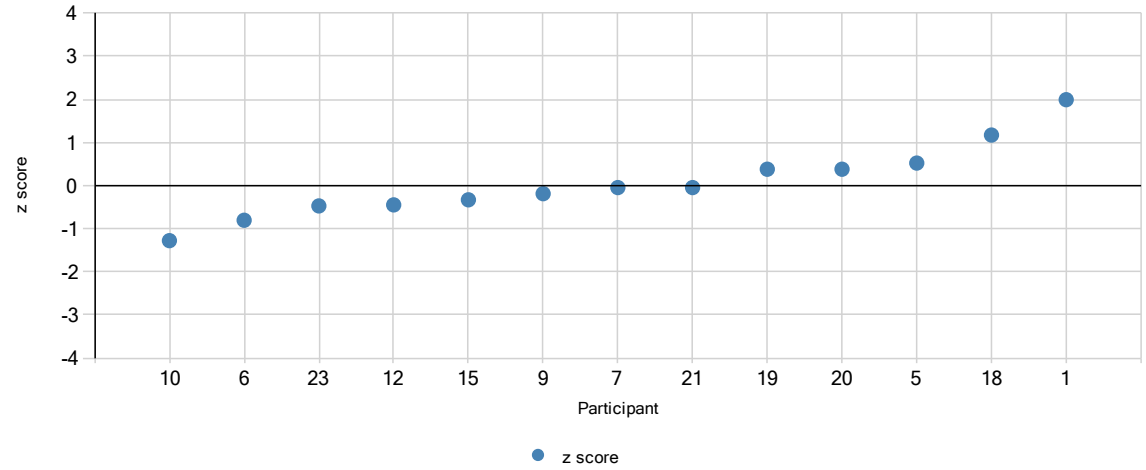
Measurand Cr Sample V4M



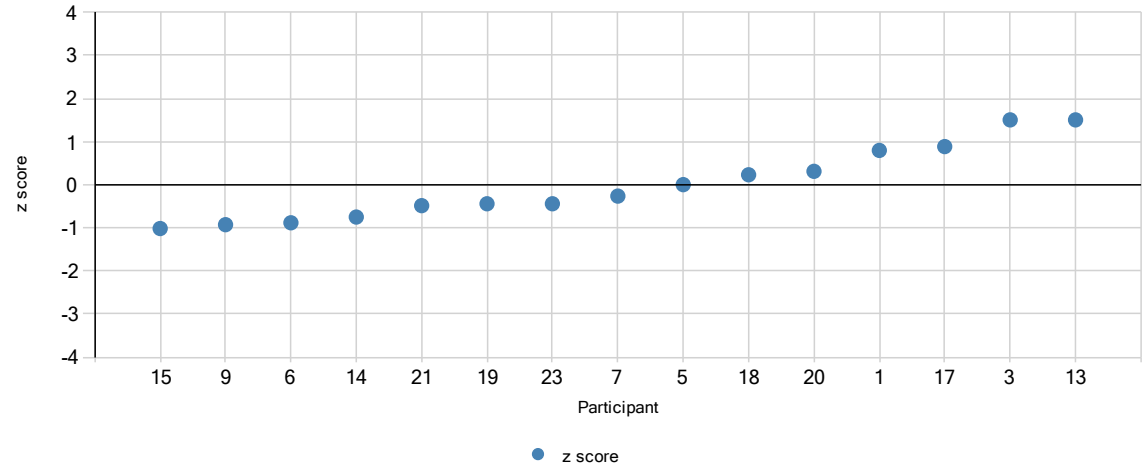
Measurand Cu Sample A1M



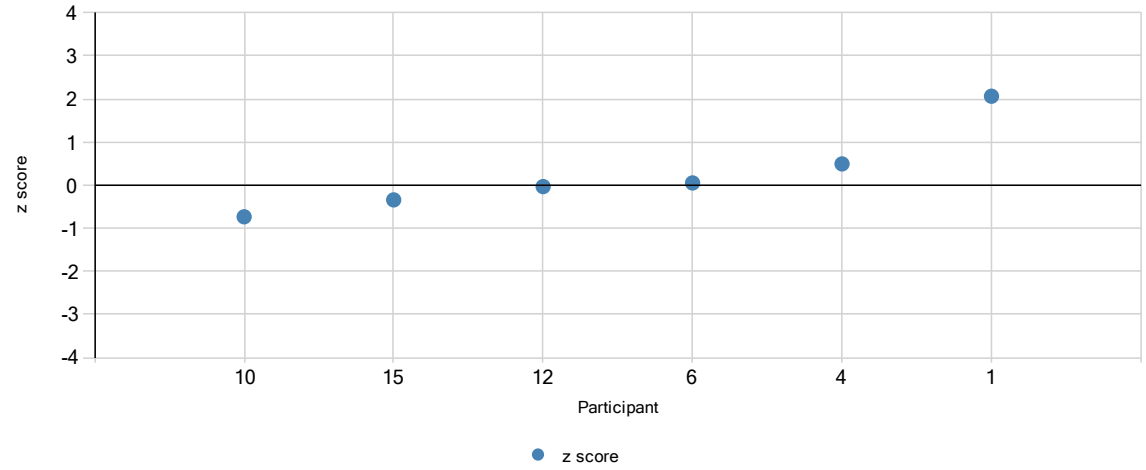
Measurand Cu Sample P2M



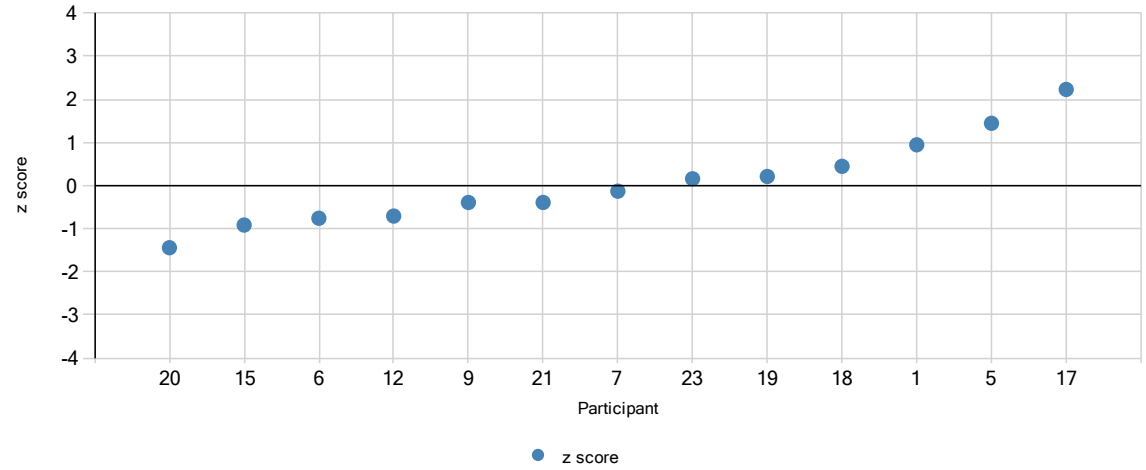
Measurand Cu Sample TN3

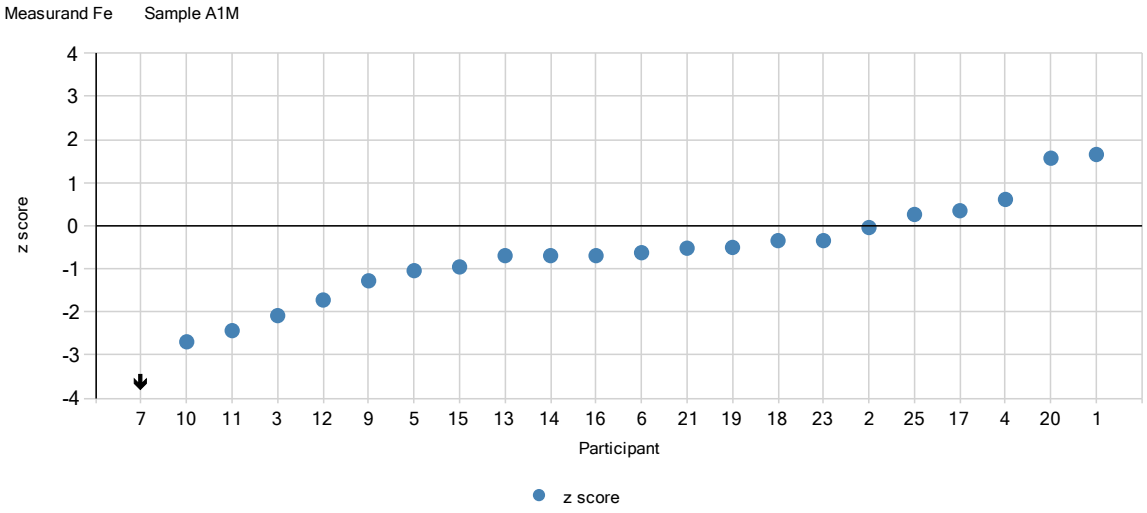


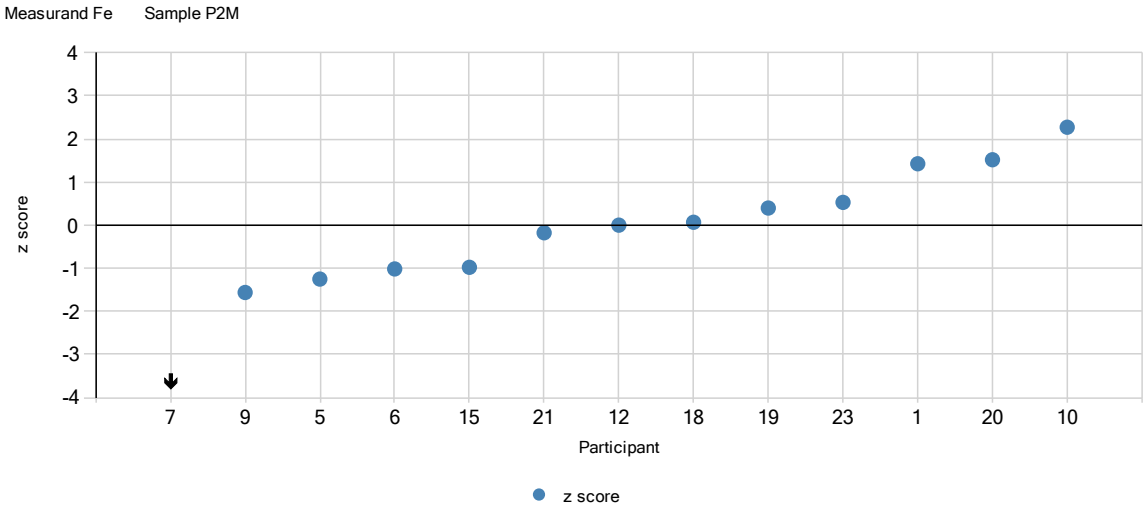
Measurand Cu Sample TY3



Measurand Cu Sample V4M




Measurand Fe Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
7 10 11 3 12 9 5 15 13 14 16 6 21 19 18 23 2 25 17 4 20 1
Participant
z score


Measurand Fe Sample P2M
z score
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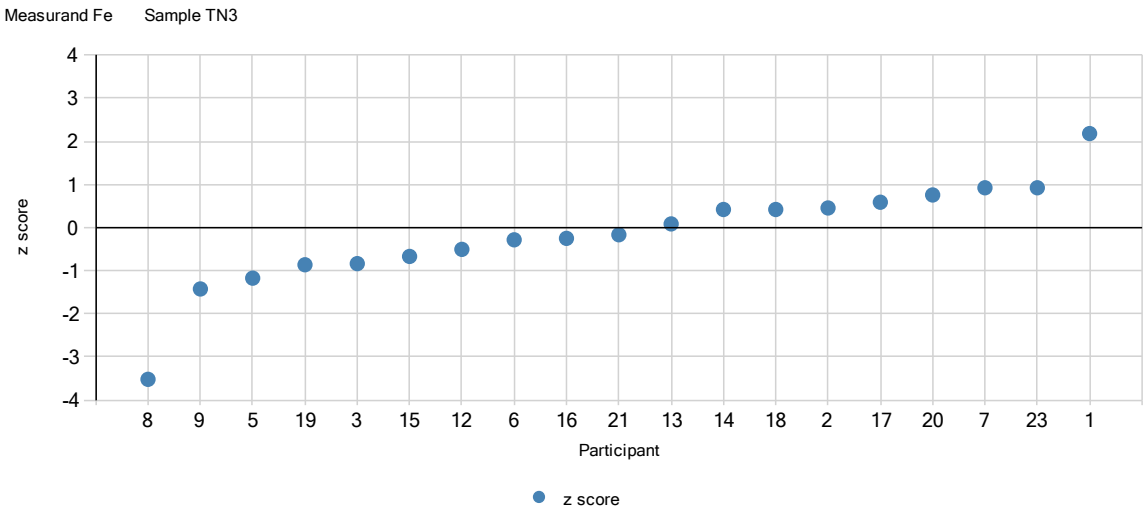
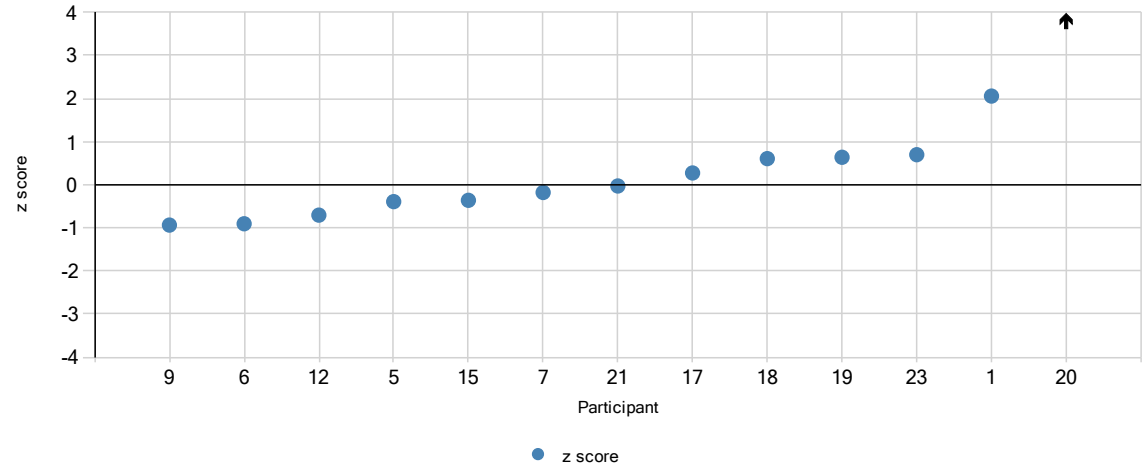
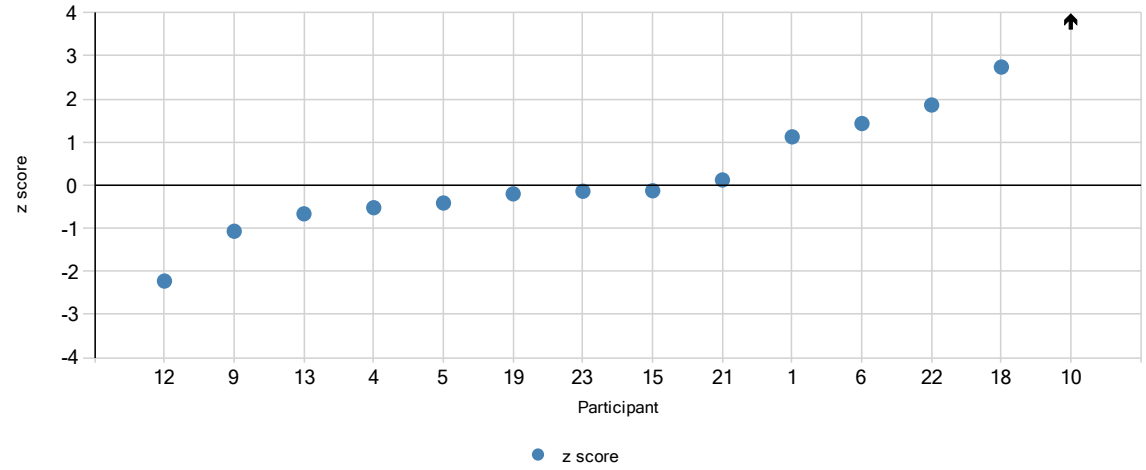
3
2
1
0
-1
-2
-3
-4
7 9 5 6 15 21 12 18 19 23 1 20 10
Participant
z score


Measurand Fe Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
8 9 5 19 3 15 12 6 16 21 13 14 18 2 17 20 7 23 1
Participant
z score

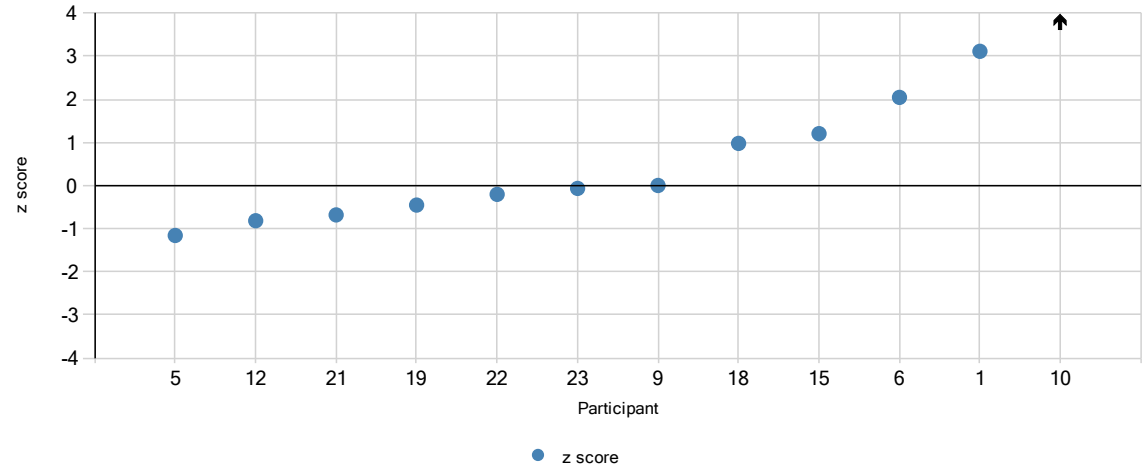
Measurand Fe Sample V4M



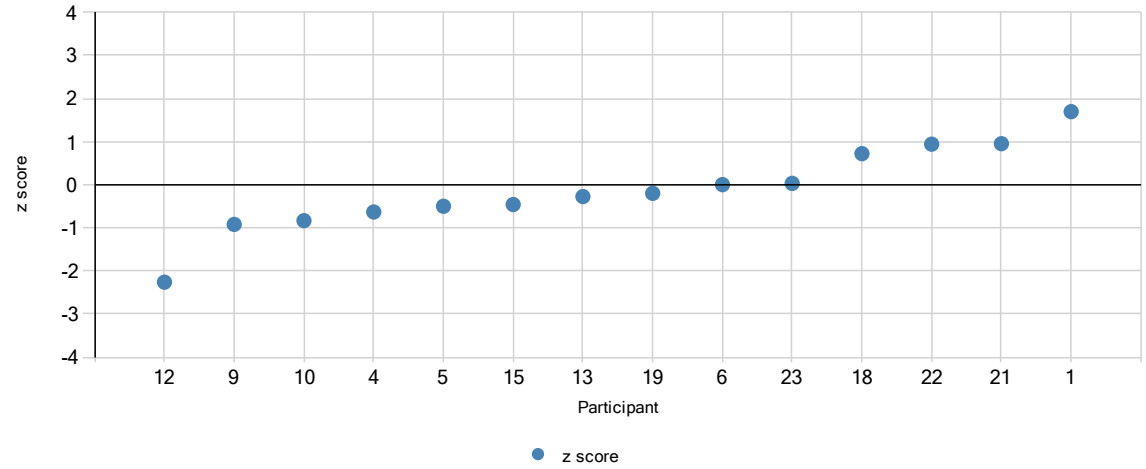
Measurand Hg Sample A1Hg



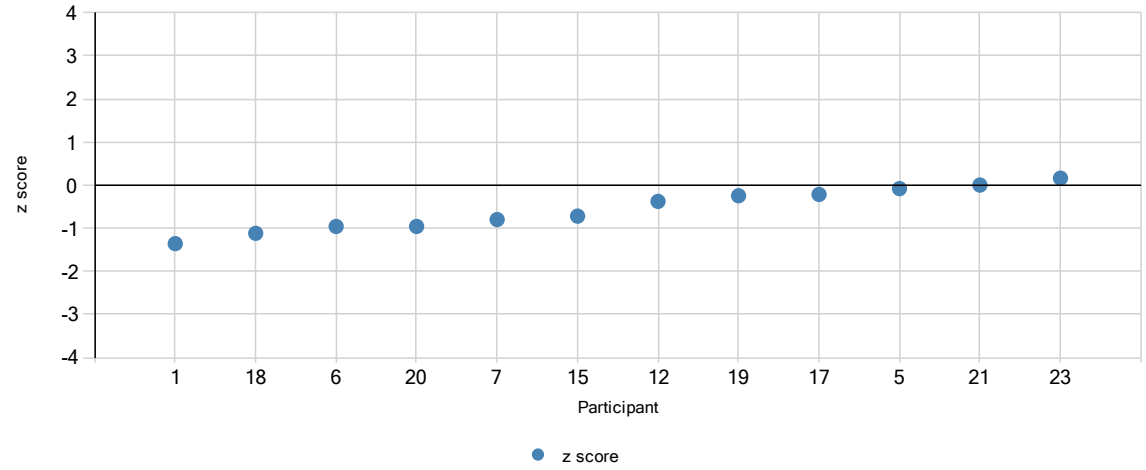
Measurand Hg Sample P2Hg



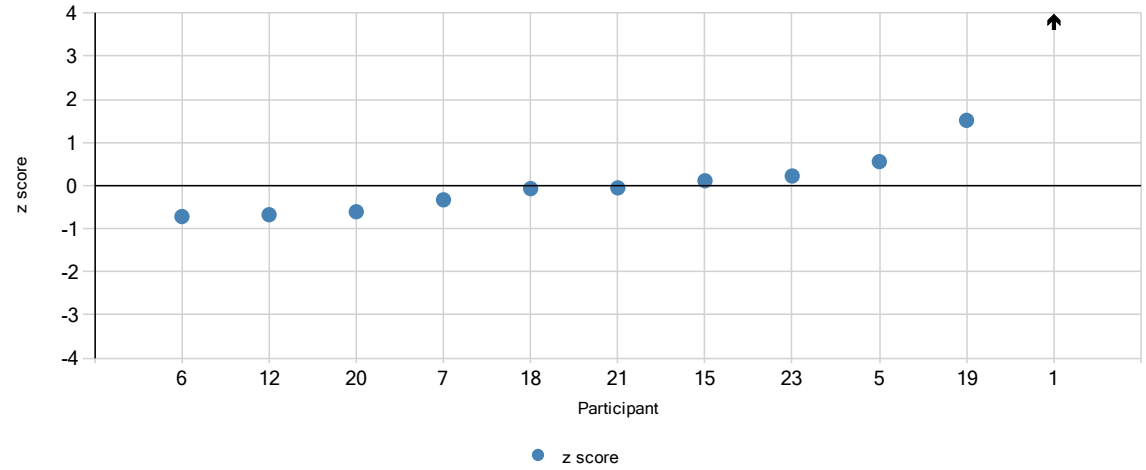
Measurand Hg Sample T3Hg



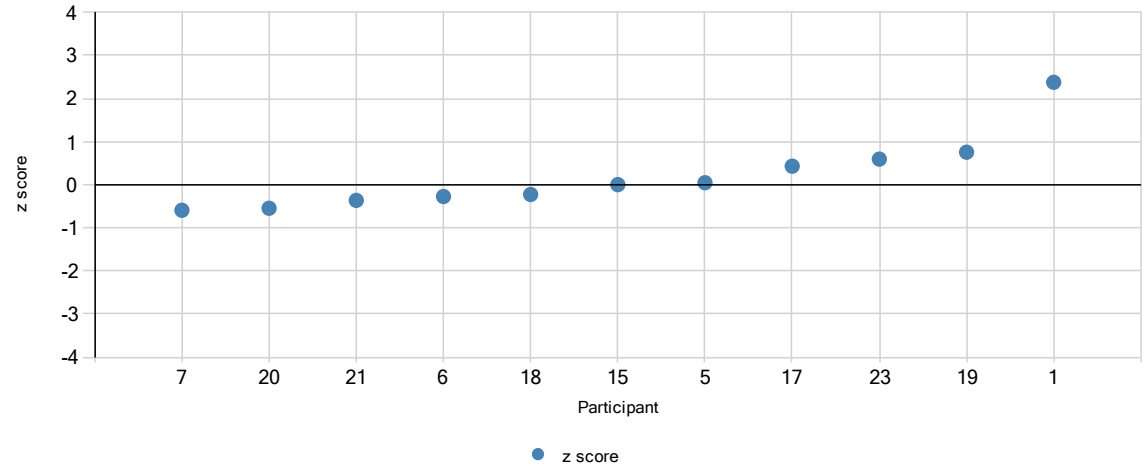
Measurand K Sample A1M



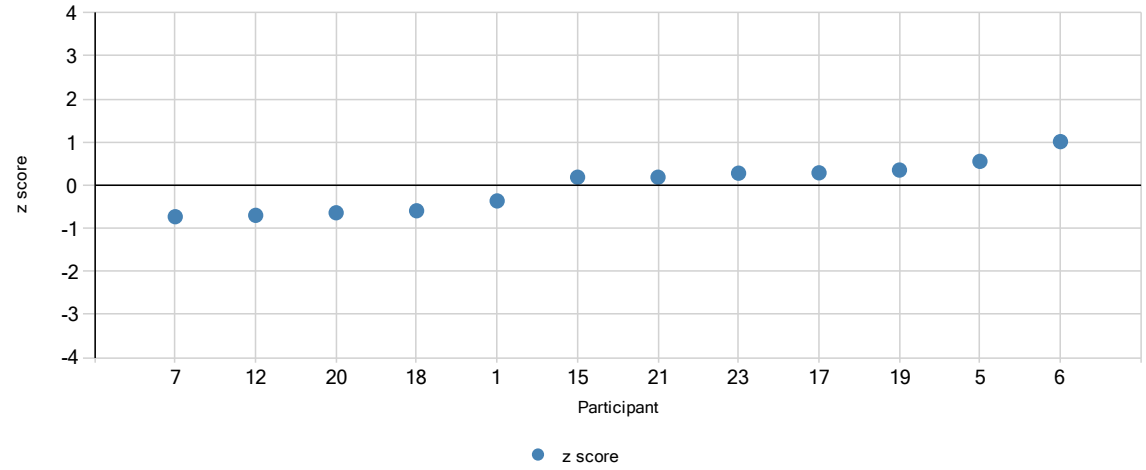
Measurand K Sample P2M



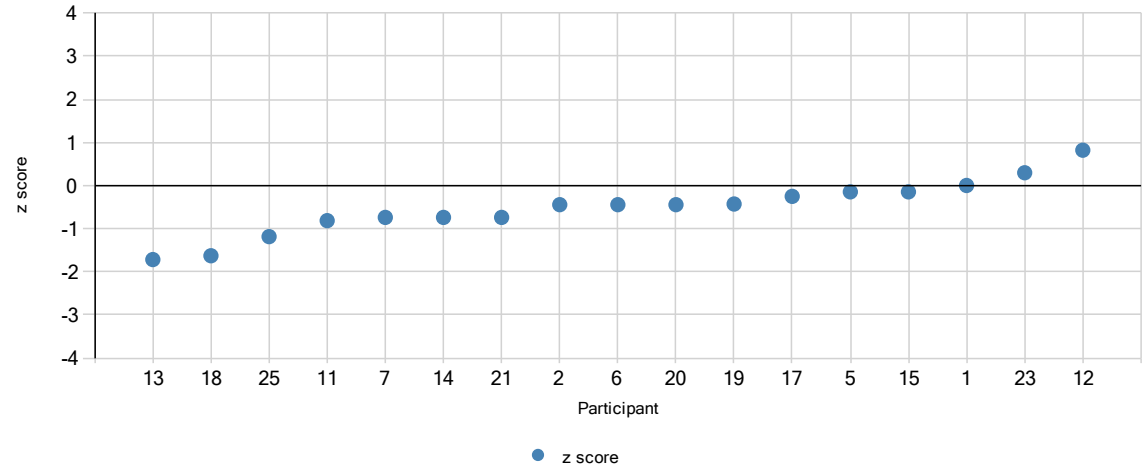
Measurand K Sample TN3

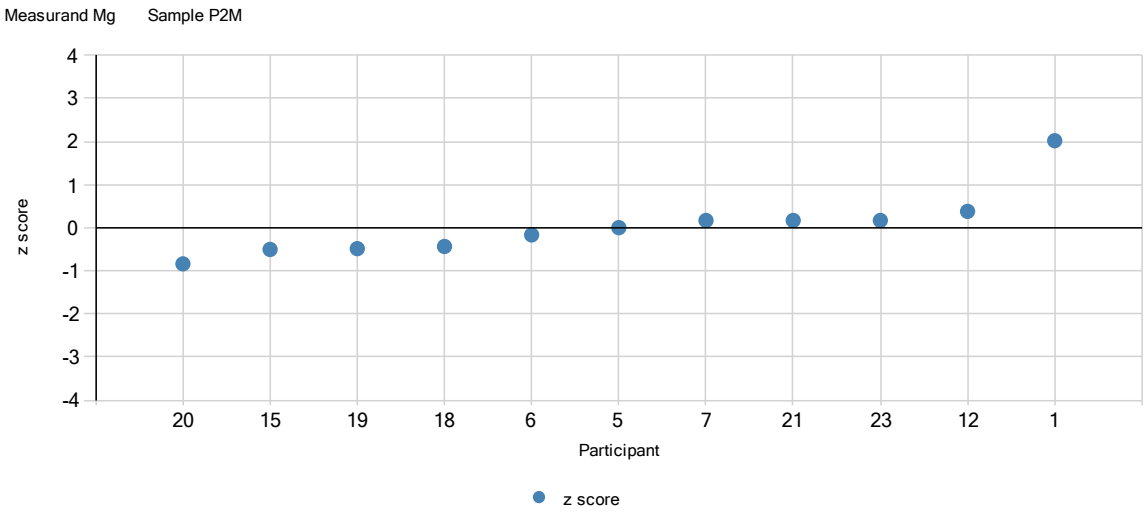


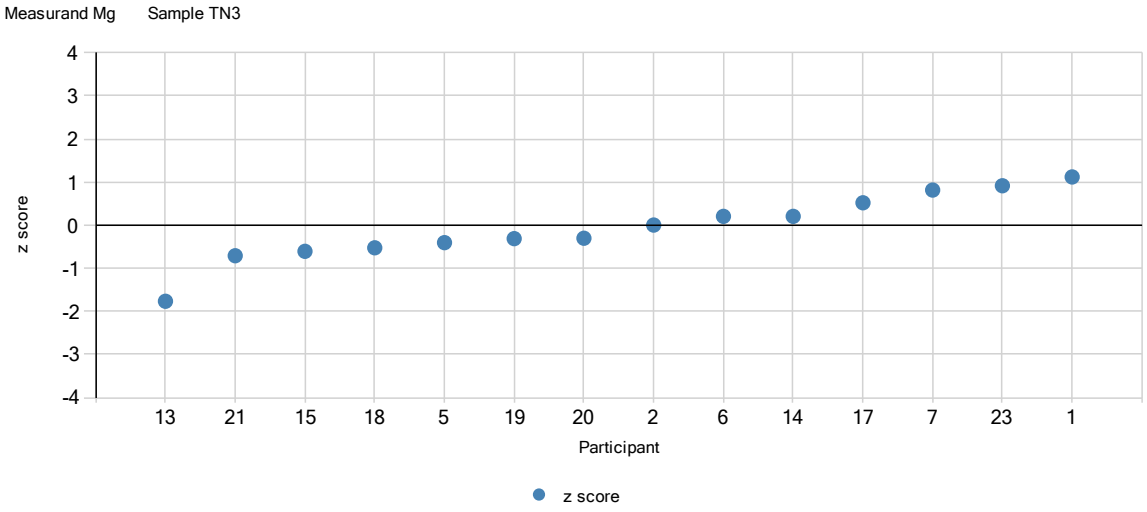
Measurand K Sample V4M



Measurand Mg Sample A1M




Measurand Mg Sample P2M
z score
4
3
2
1
0
-1
-2
-3
-4
20 15 19 18 6 5 7 21 23 12 1
Participant
z score


Measurand Mg Sample TN3
z score
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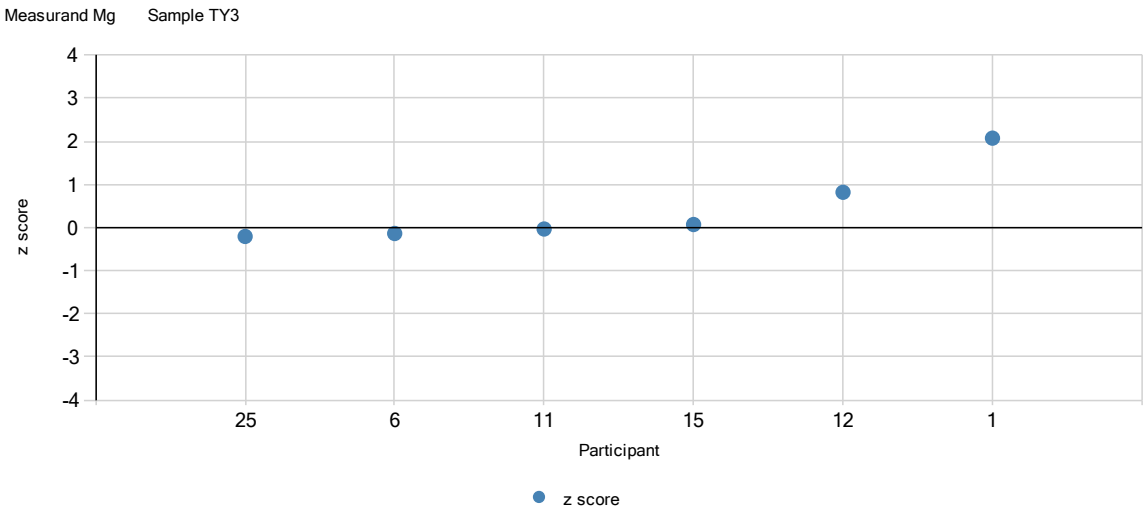
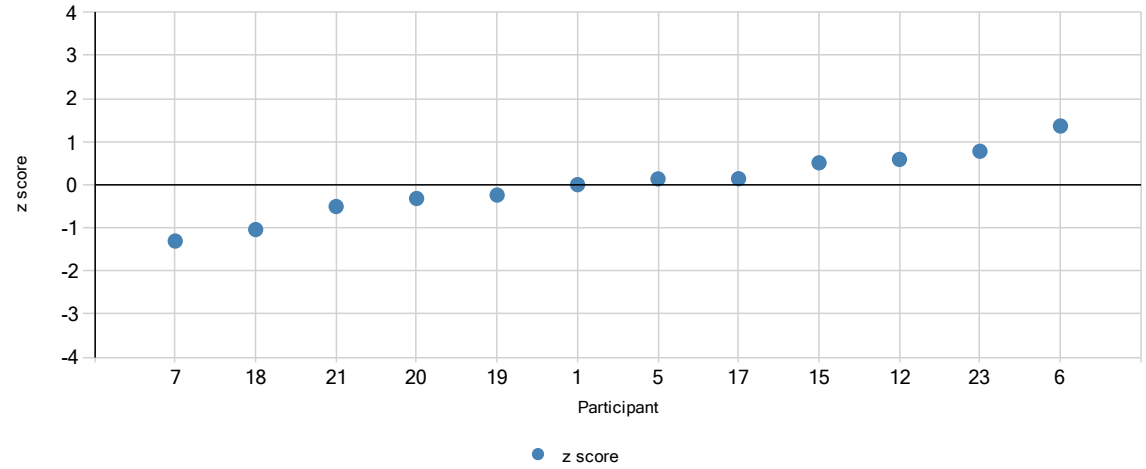
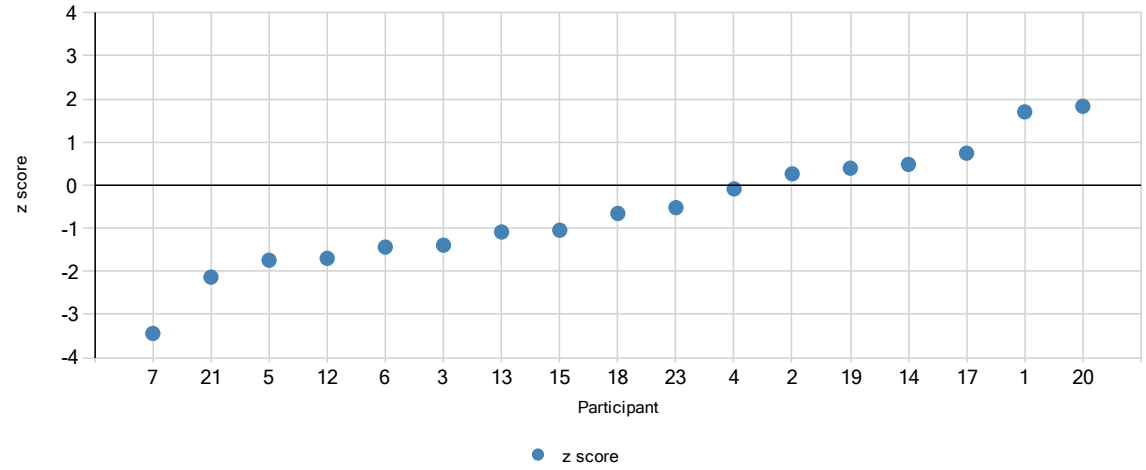
3
2
1
0
-1
-2
-3
-4
13 21 15 18 5 19 20 2 6 14 17 7 23 1
Participant
z score


Measurand Mg Sample TY3
z score
4
3
2
1
0
-1
-2
-3
-4
25 6 11 15 12 1
Participant
z score

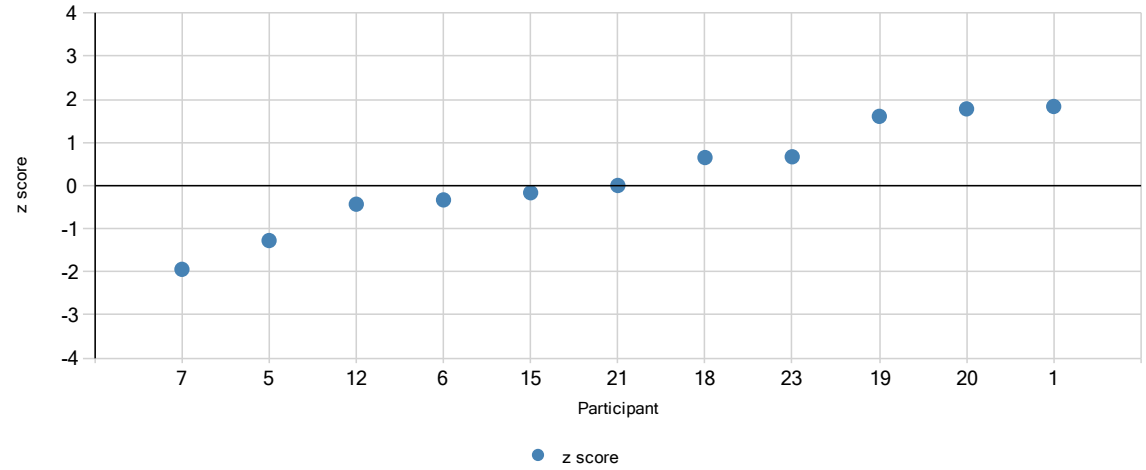
Measurand Mg Sample V4M



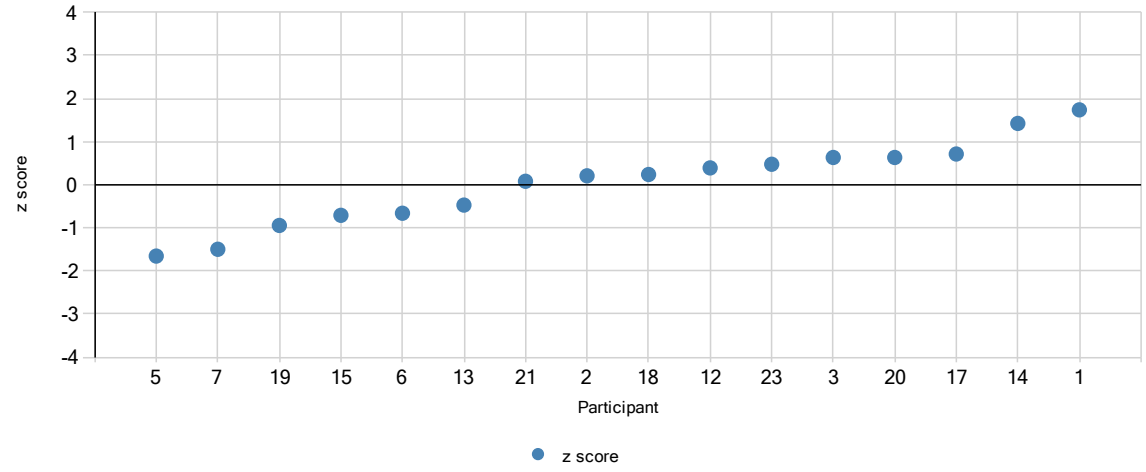
Measurand Mn Sample A1M



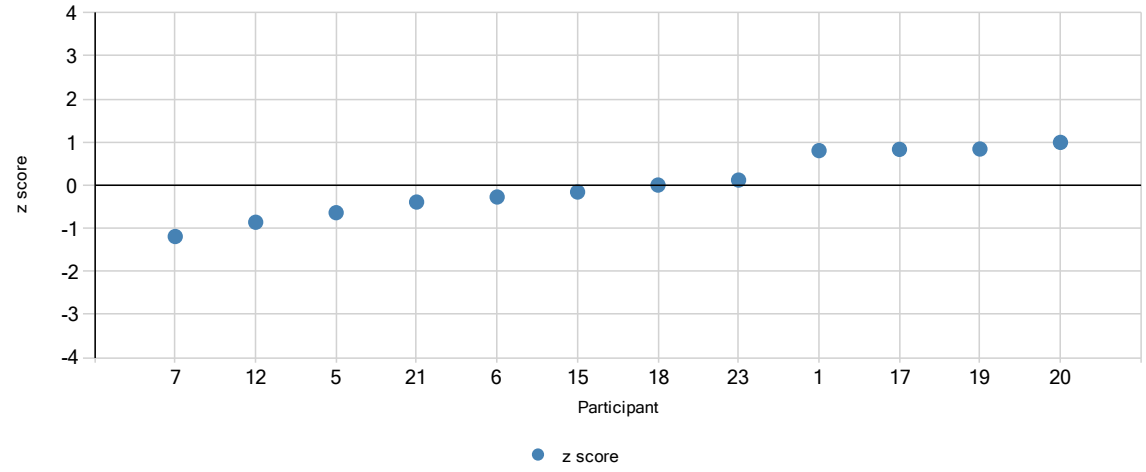
Measurand Mn Sample P2M



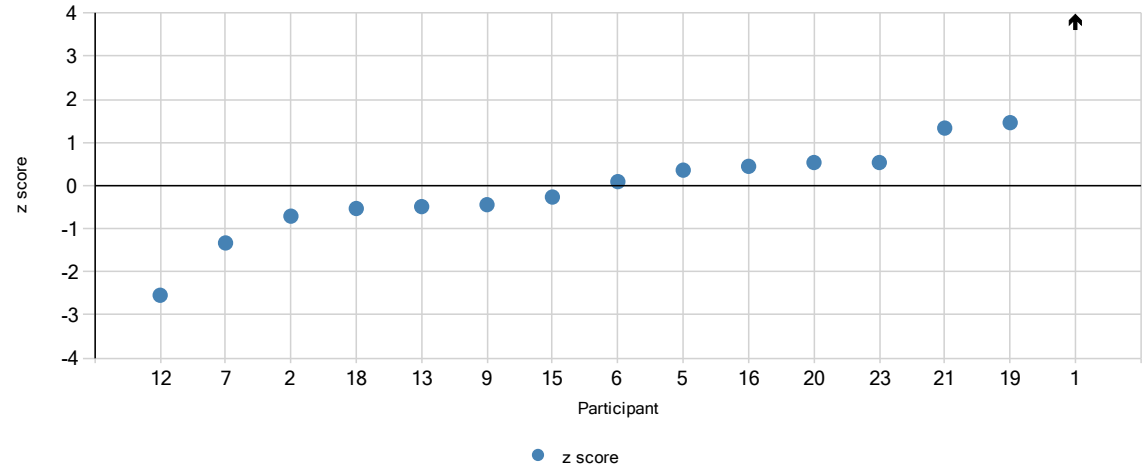
Measurand Mn Sample TN3



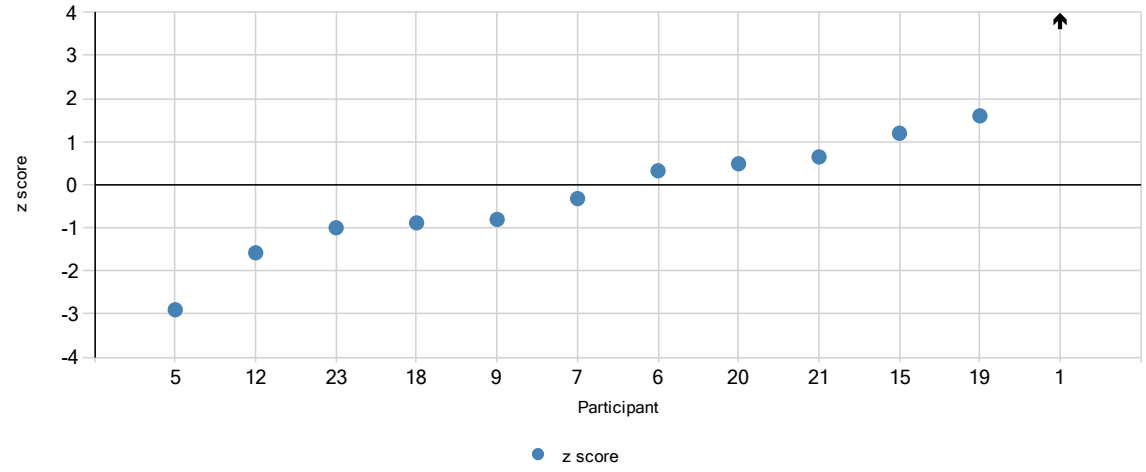
Measurand Mn Sample V4M



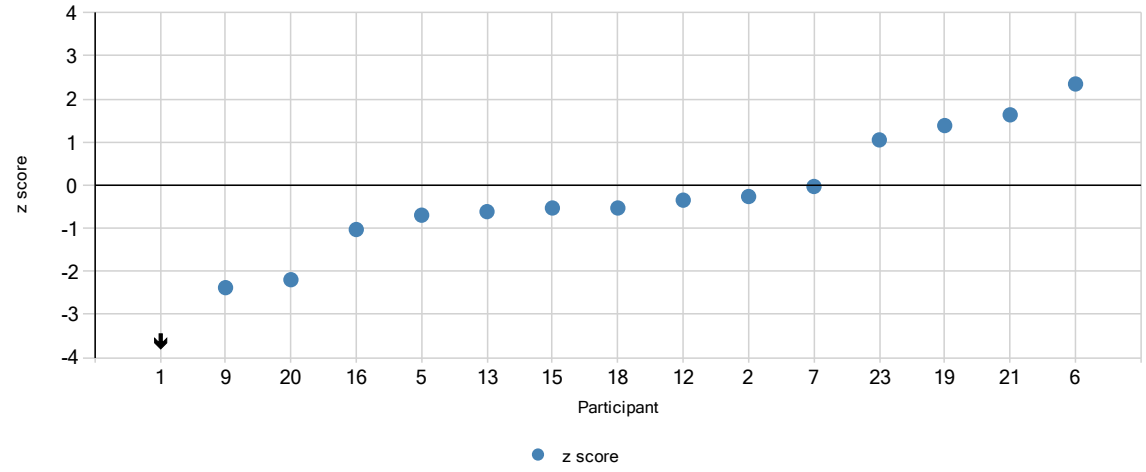
Measurand Mo Sample A1M



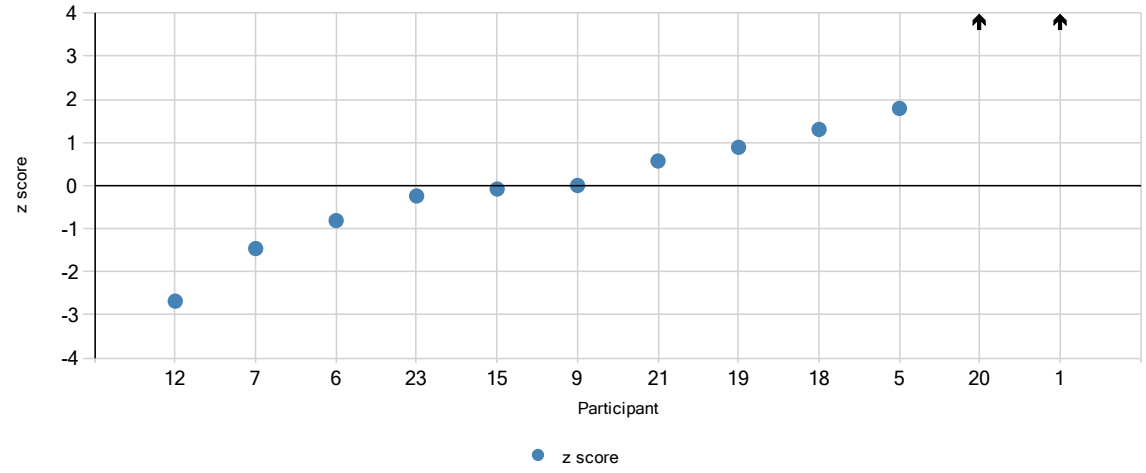
Measurand Mo Sample P2M

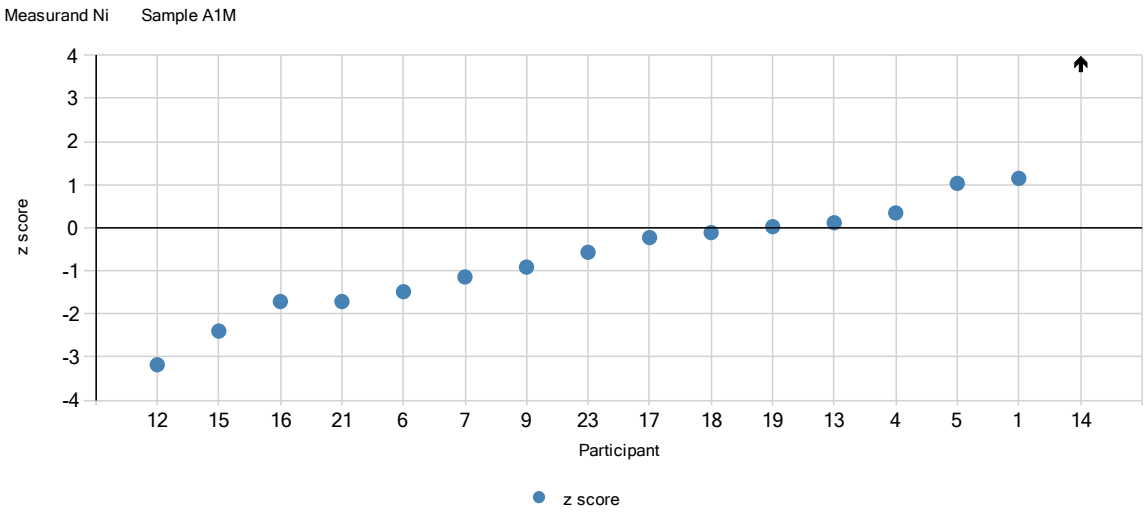


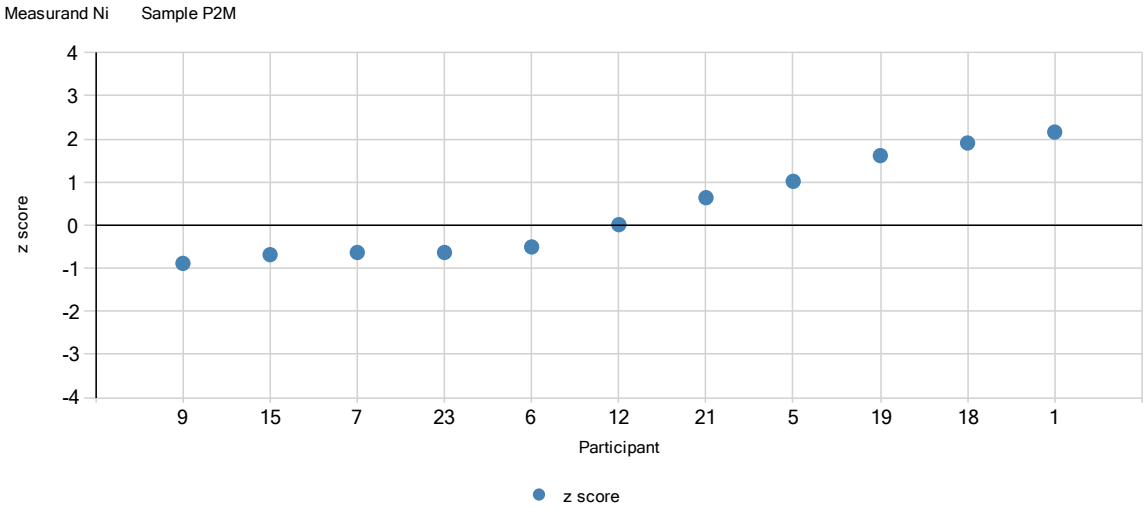
Measurand Mo Sample TN3

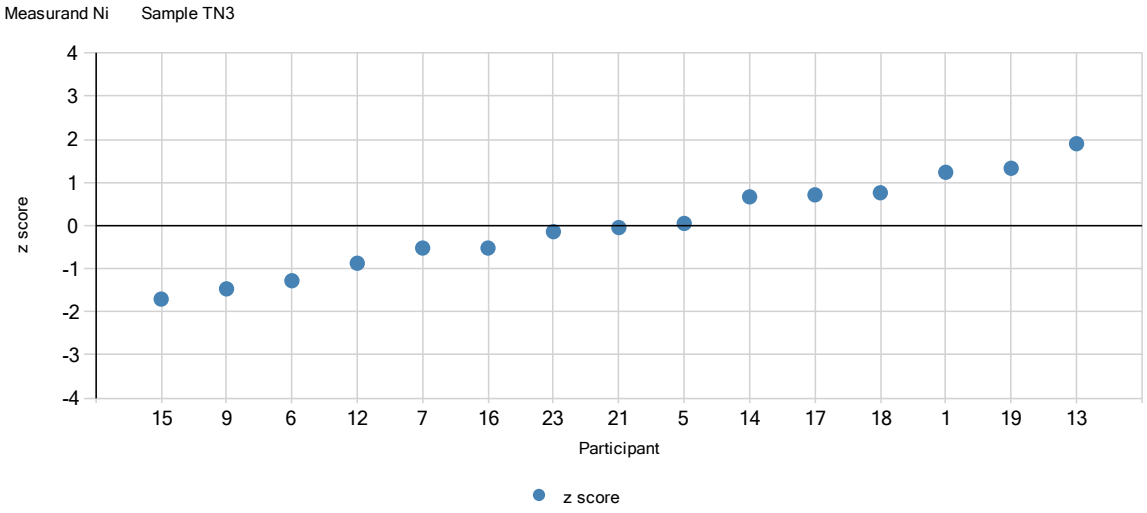


Measurand Mo Sample V4M

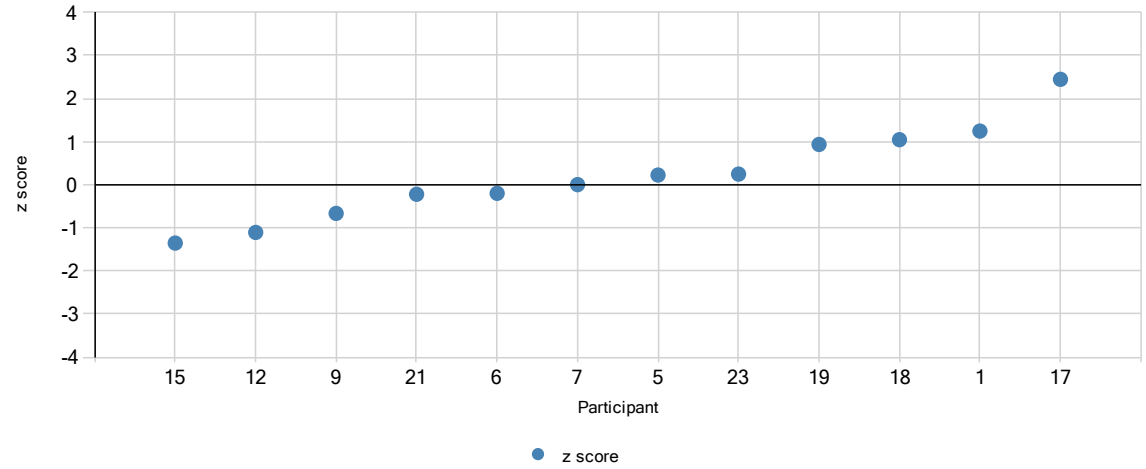



Measurand Ni
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
12 15 16 21 6 7 9 23 17 18 19 13 4 5 1 14
Participant
z score

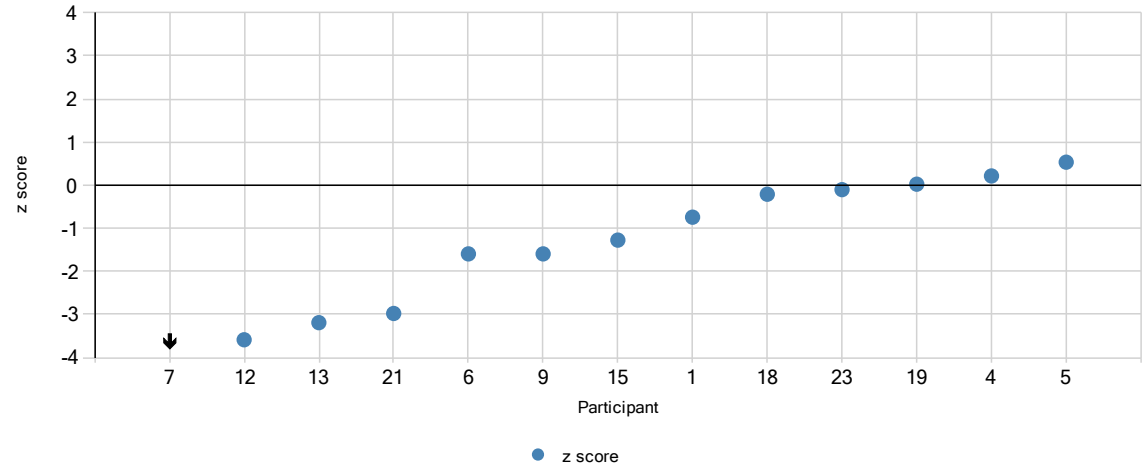

Measurand Ni
Sample P2M
z score
4
3
2
1
0
-1
-2
-3
-4
9 15 7 23 6 12 21 5 19 18 1
Participant
z score


Measurand Ni
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
15 9 6 12 7 16 23 21 5 14 17 18 1 19 13
Participant
z score

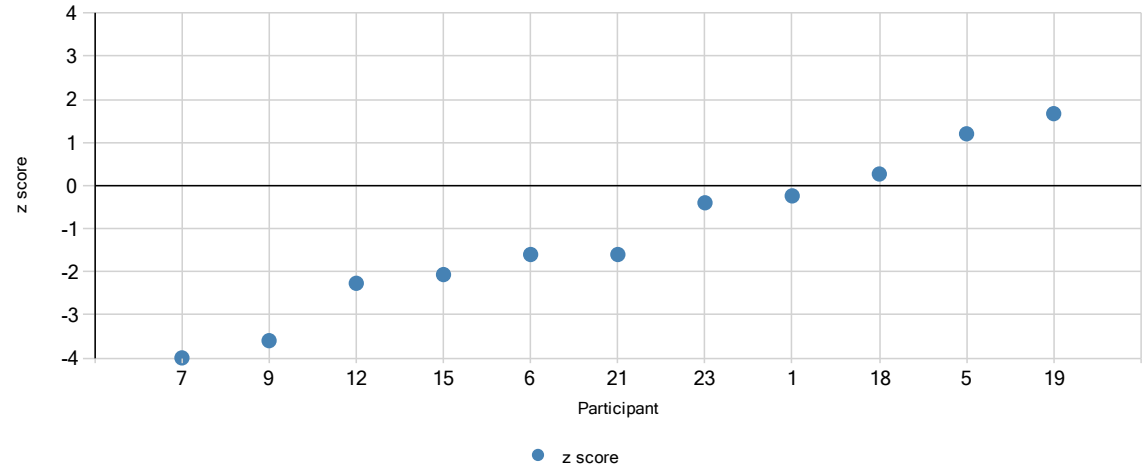
Measurand Ni Sample V4M



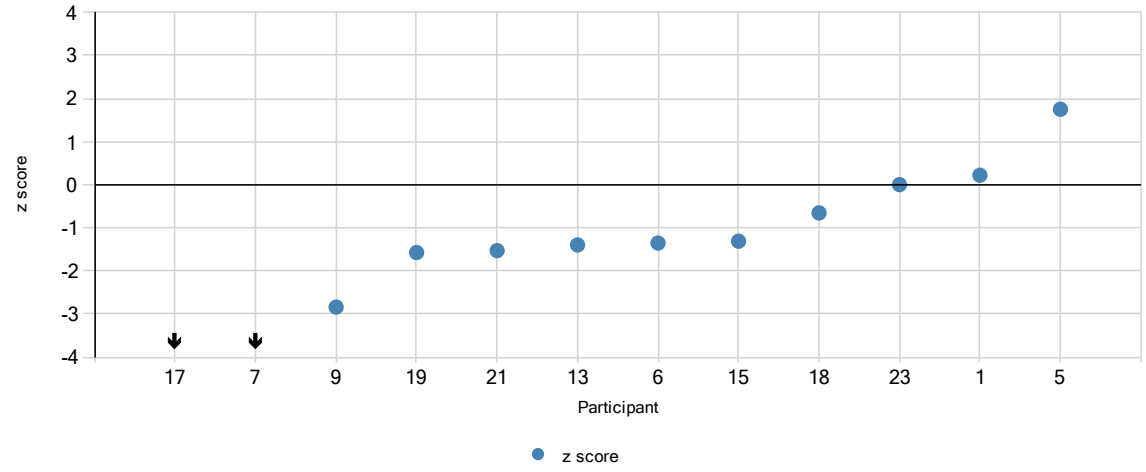
Measurand Pb Sample A1M



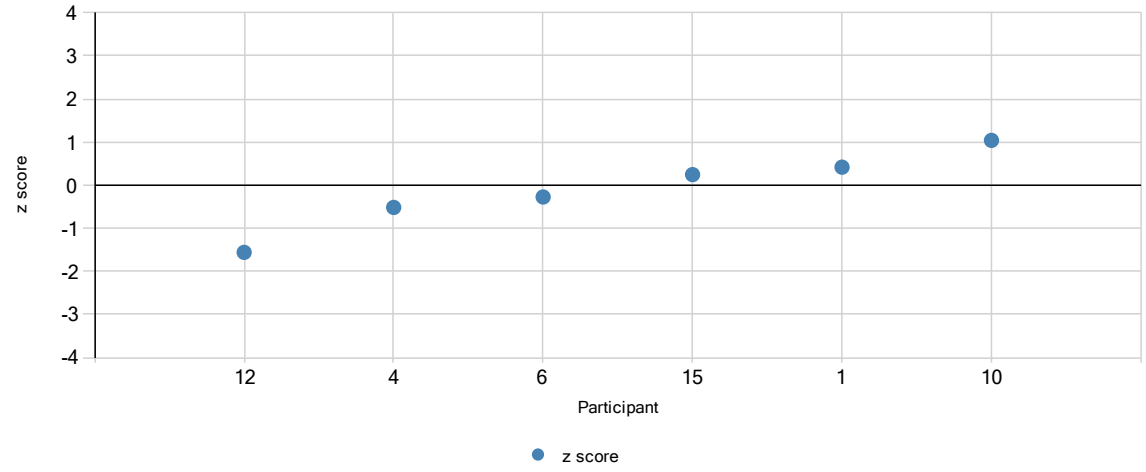
Measurand Pb Sample P2M



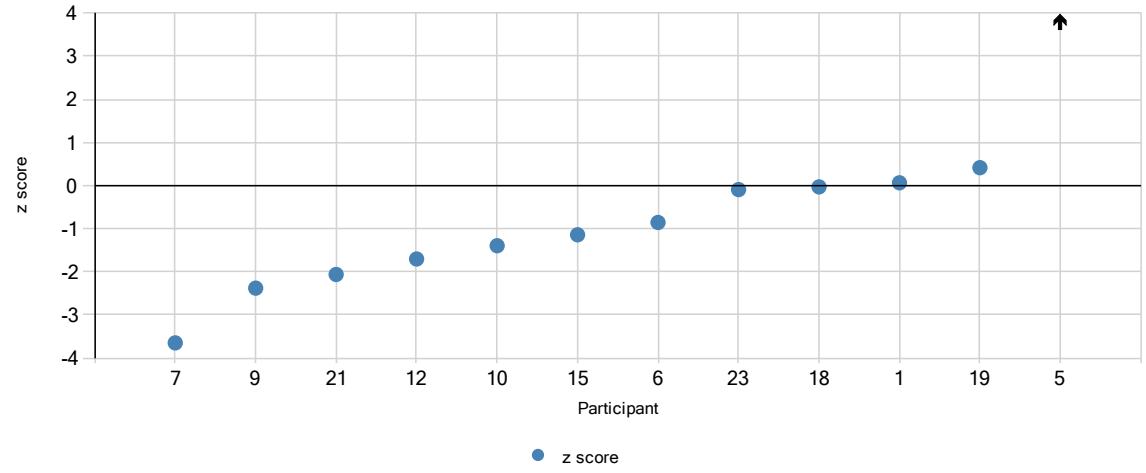
Measurand Pb Sample TN3



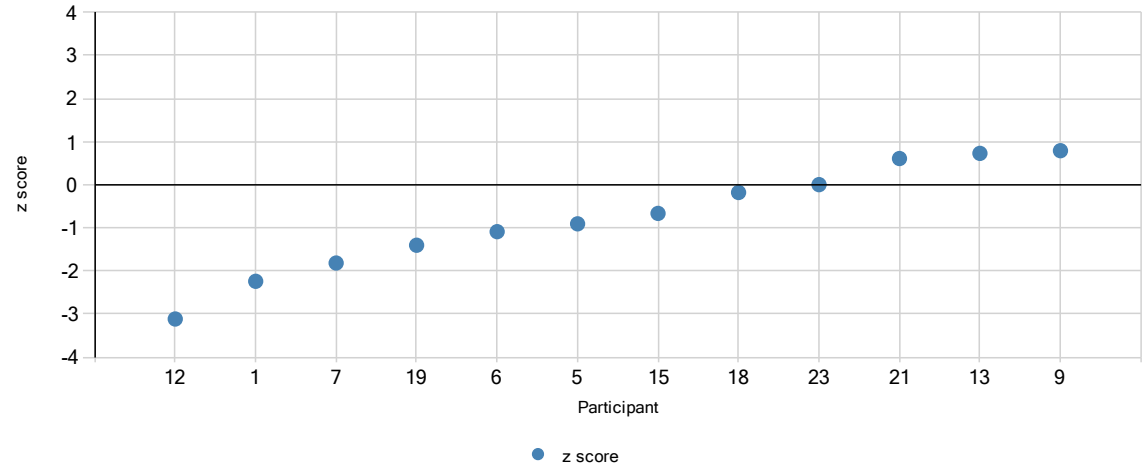
Measurand Pb Sample TY3



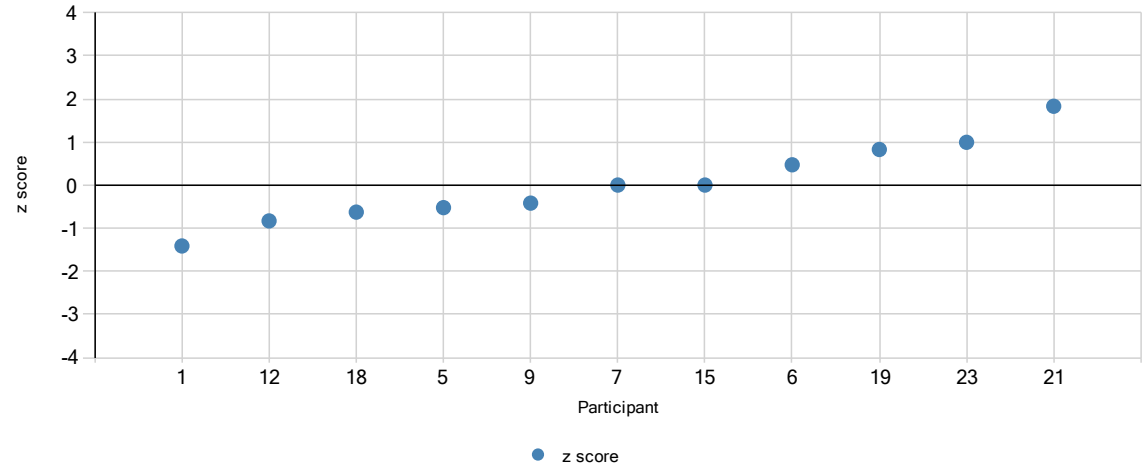
Measurand Pb Sample V4M



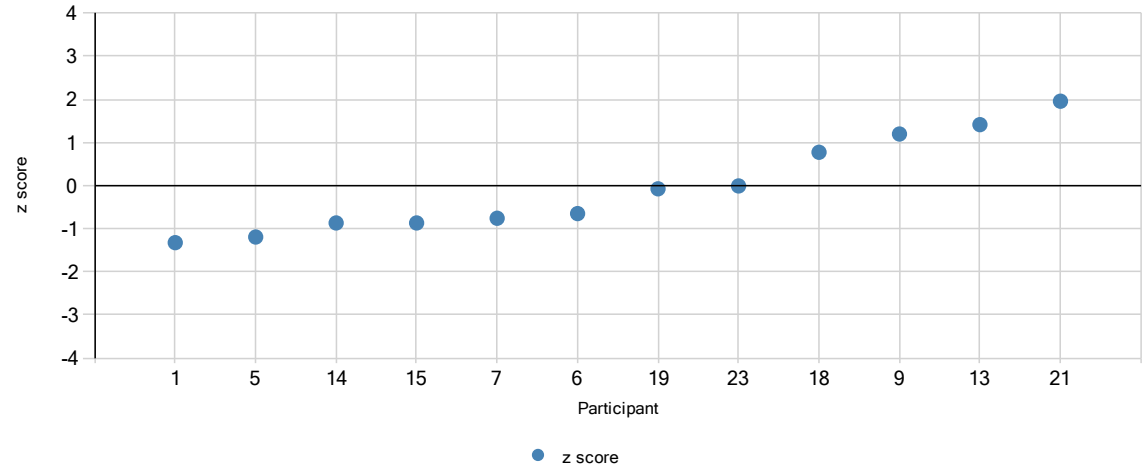
Measurand Sb Sample A1M

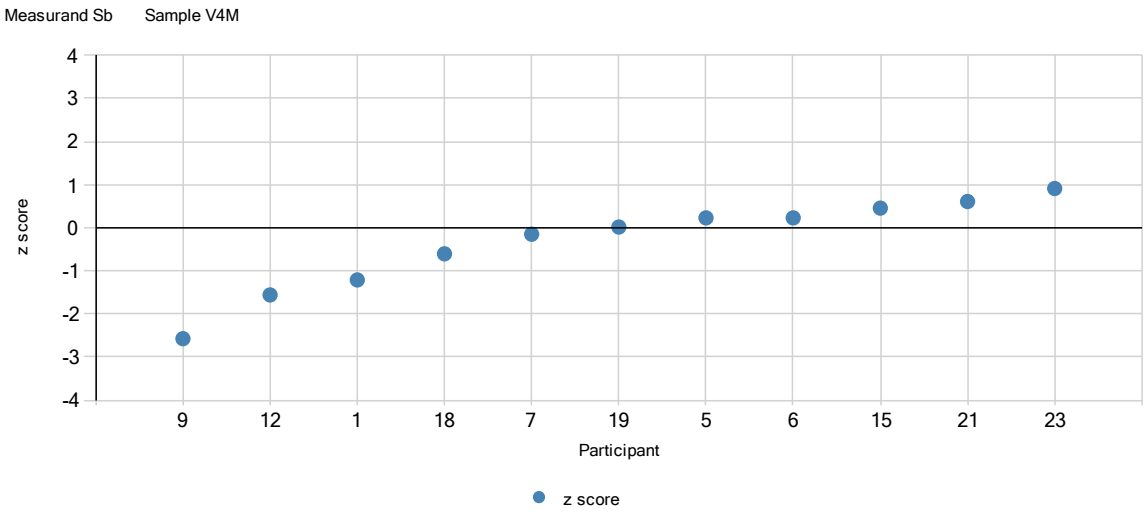


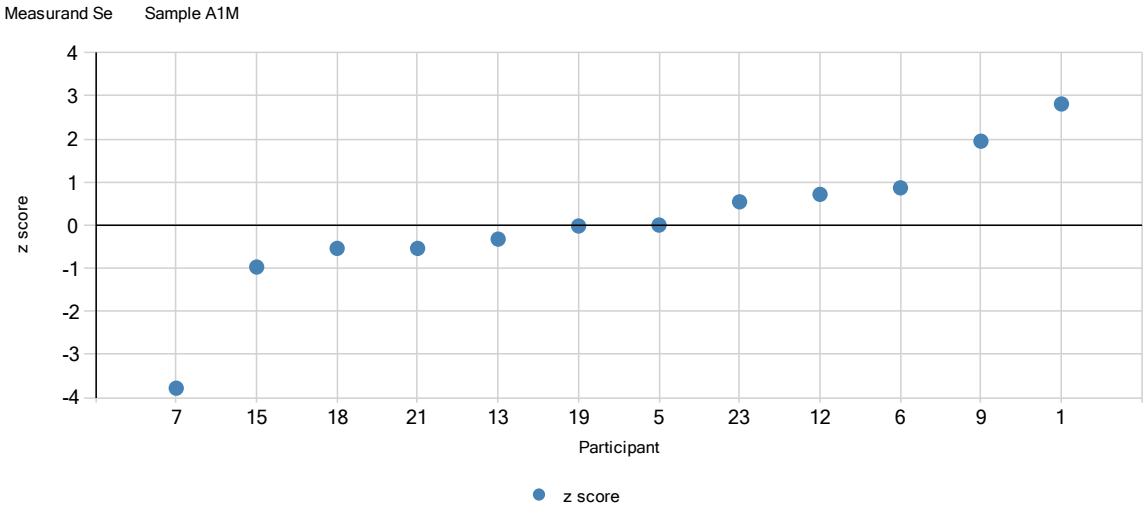
Measurand Sb Sample P2M

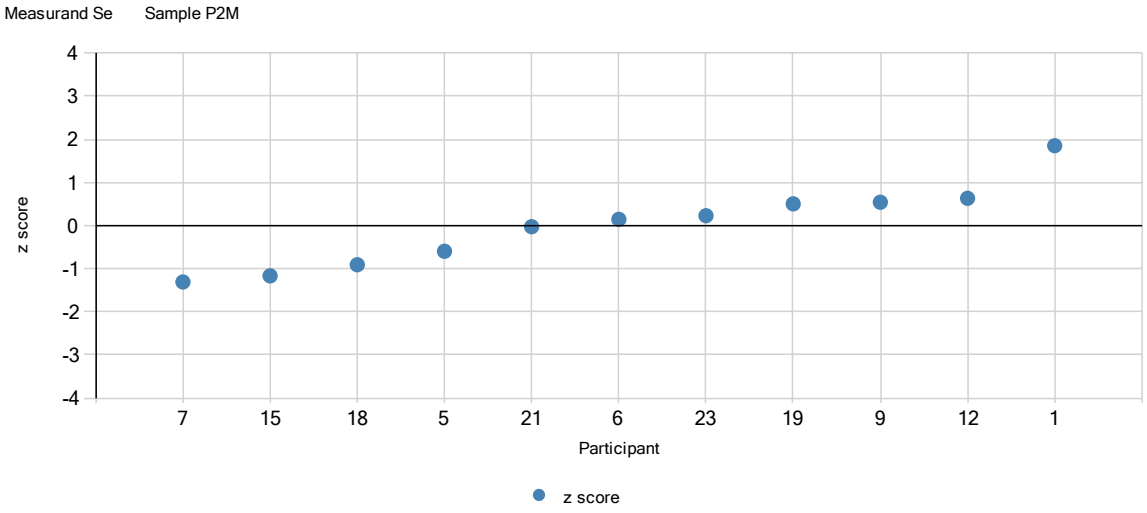


Measurand Sb Sample TN3

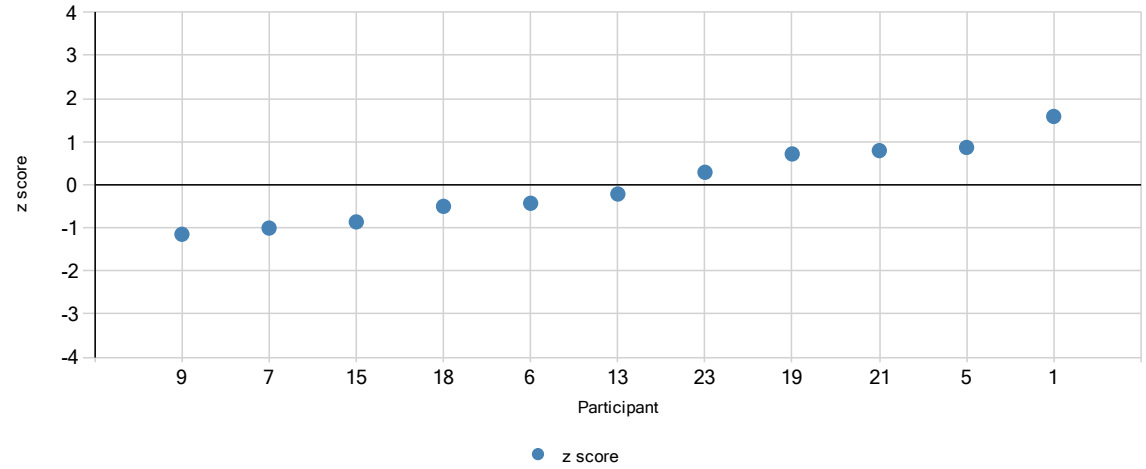



Measurand Sb Sample V4M
z score
4
3
2
1
0
-1
-2
-3
-4
9 12 1 18 7 19 5 6 15 21 23
Participant
z score

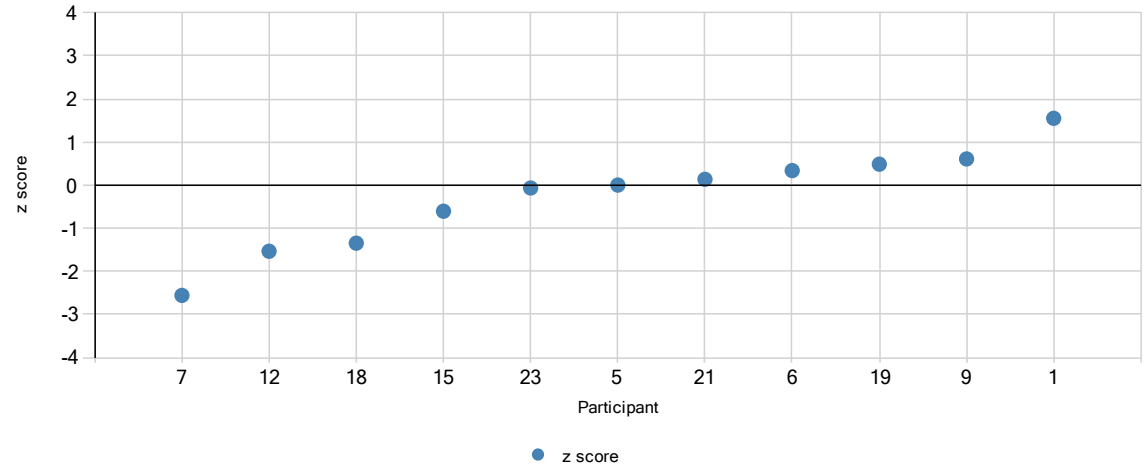

Measurand Se Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
7 15 18 21 13 19 5 23 12 6 9 1
Participant
z score


Measurand Se Sample P2M
z score
4
3
2
1
0
-1
-2
-3
-4
7 15 18 5 21 6 23 19 9 12 1
Participant
z score

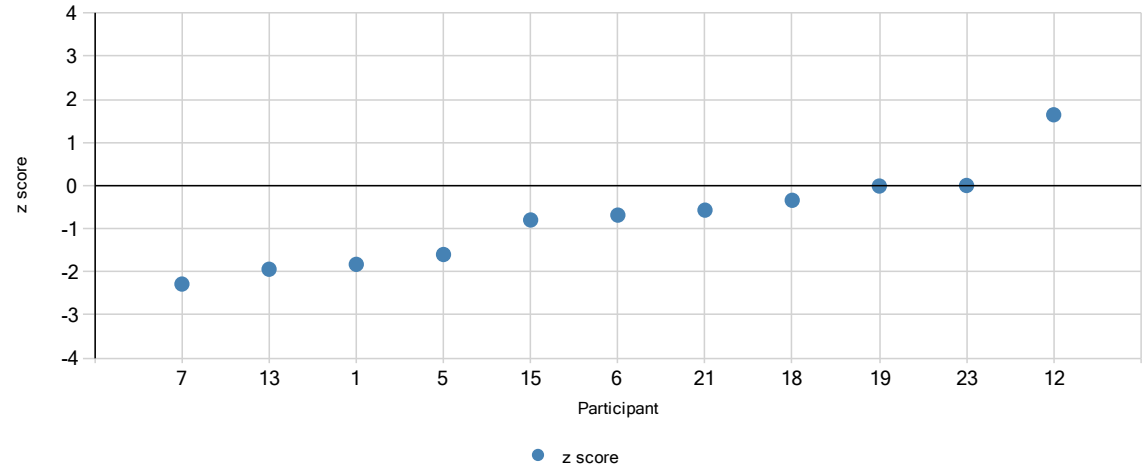
Measurand Se Sample TN3

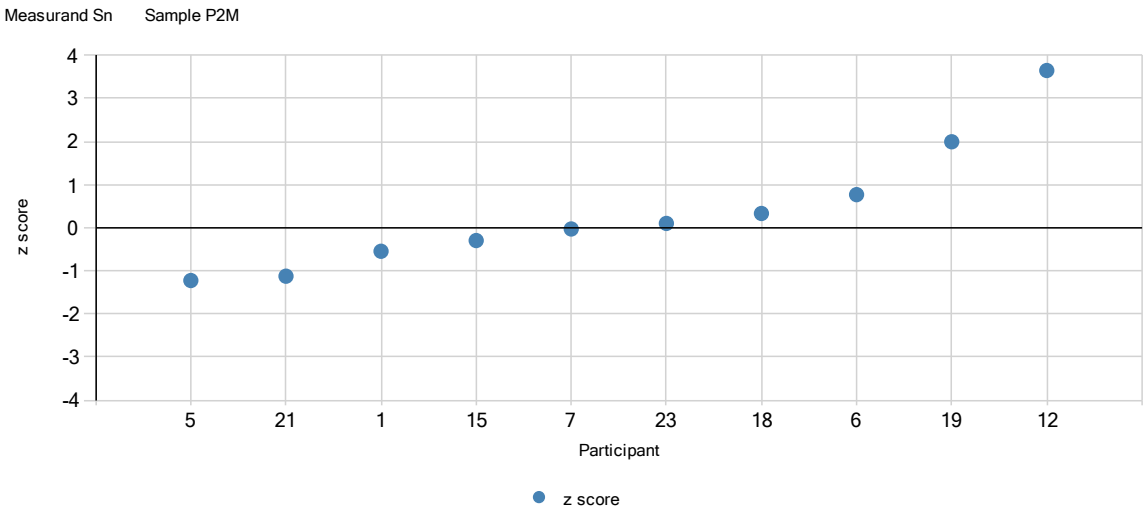


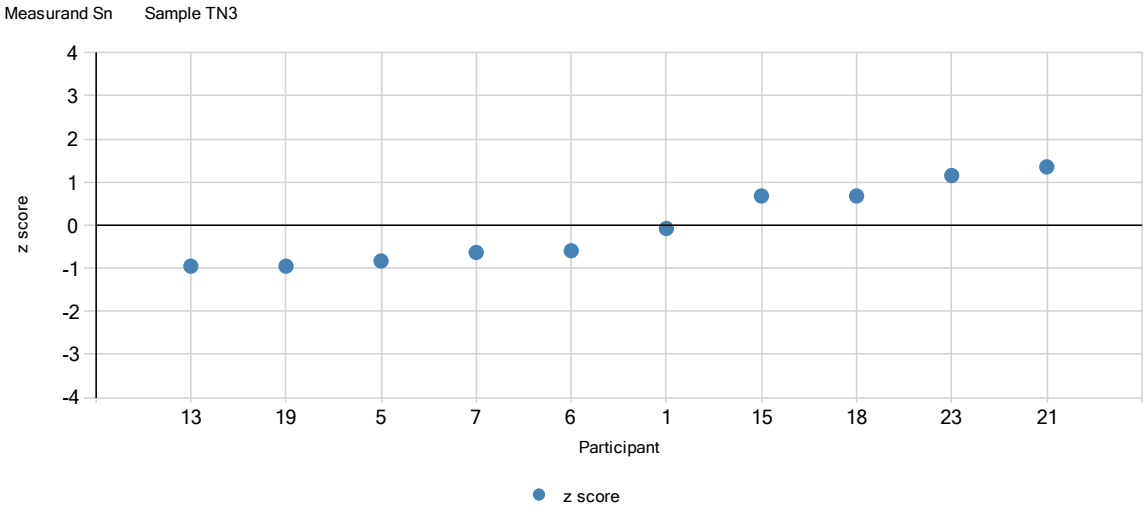
Measurand Se Sample V4M

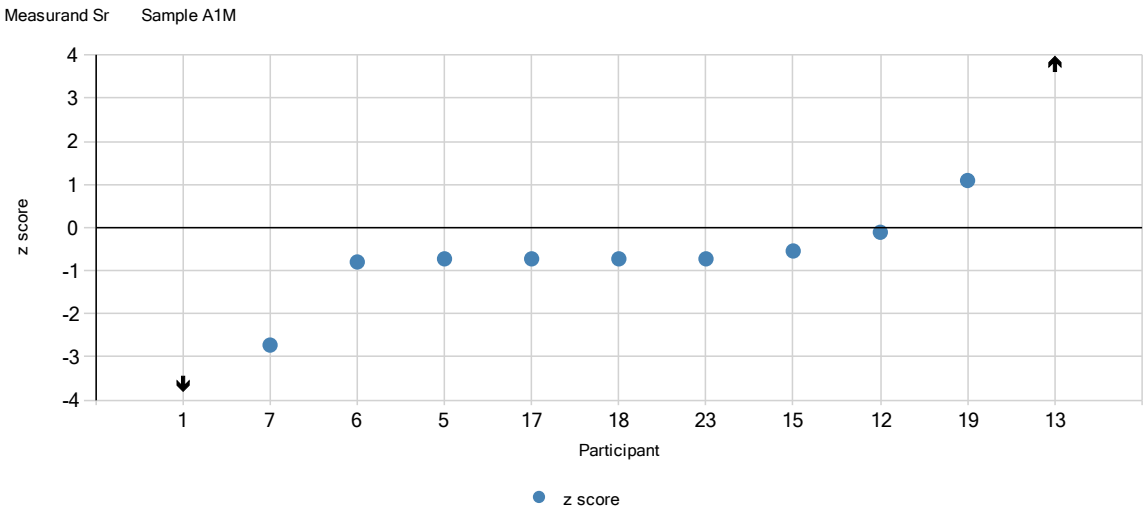


Measurand Sn Sample A1M

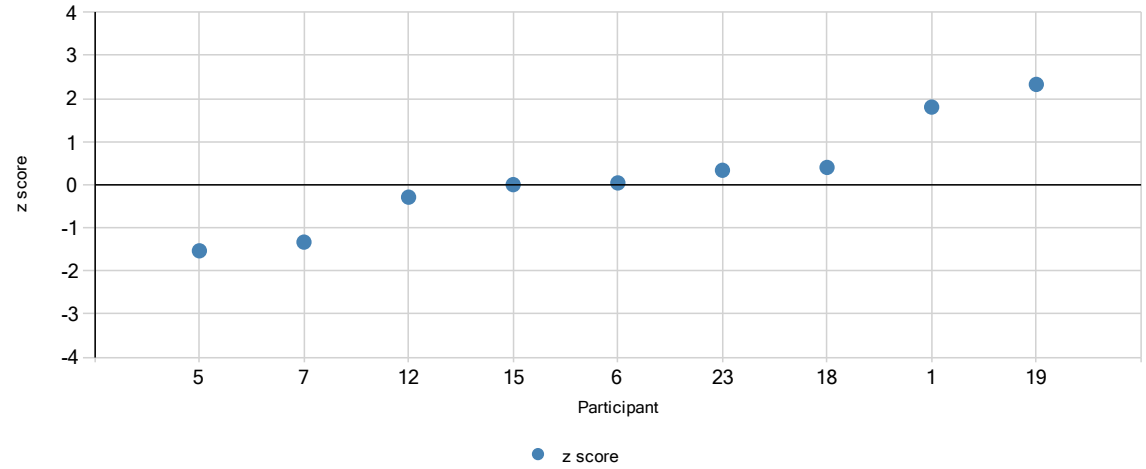



Measurand Sn Sample P2M
z score
4
3
2
1
0
-1
-2
-3
-4
5 21 1 15 7 23 18 6 19 12
Participant
z score

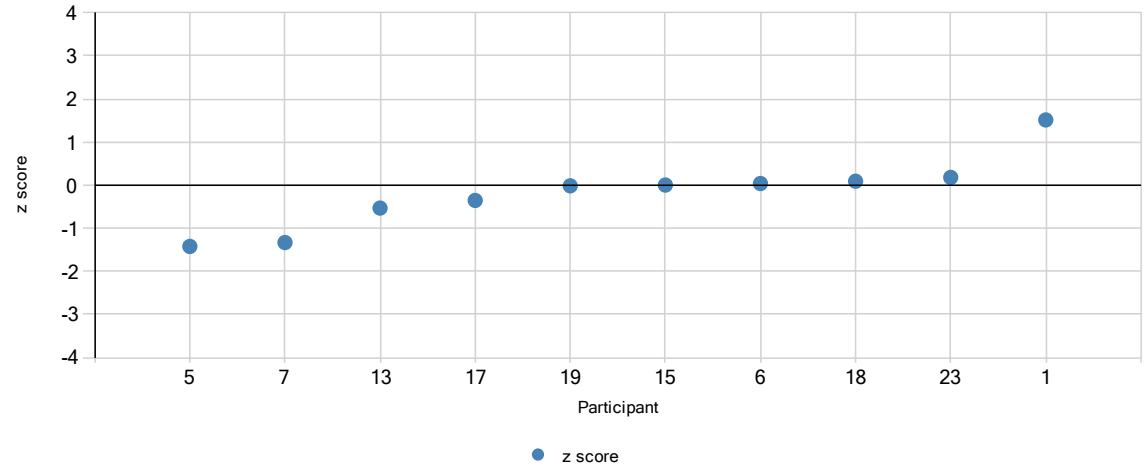

Measurand Sn Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
13 19 5 7 6 1 15 18 23 21
Participant
z score


Measurand Sr Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
1 7 6 5 17 18 23 15 12 19 13
Participant
z score

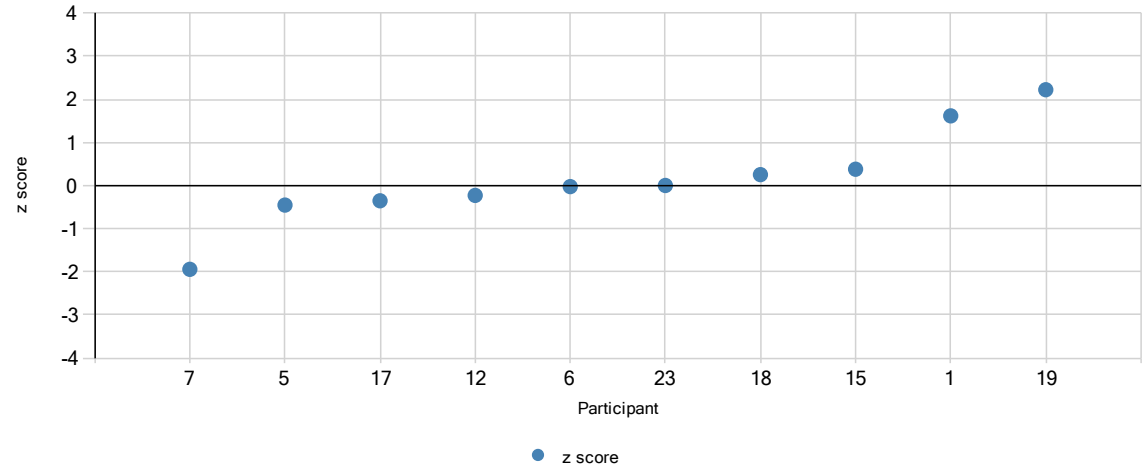
Measurand Sr Sample P2M

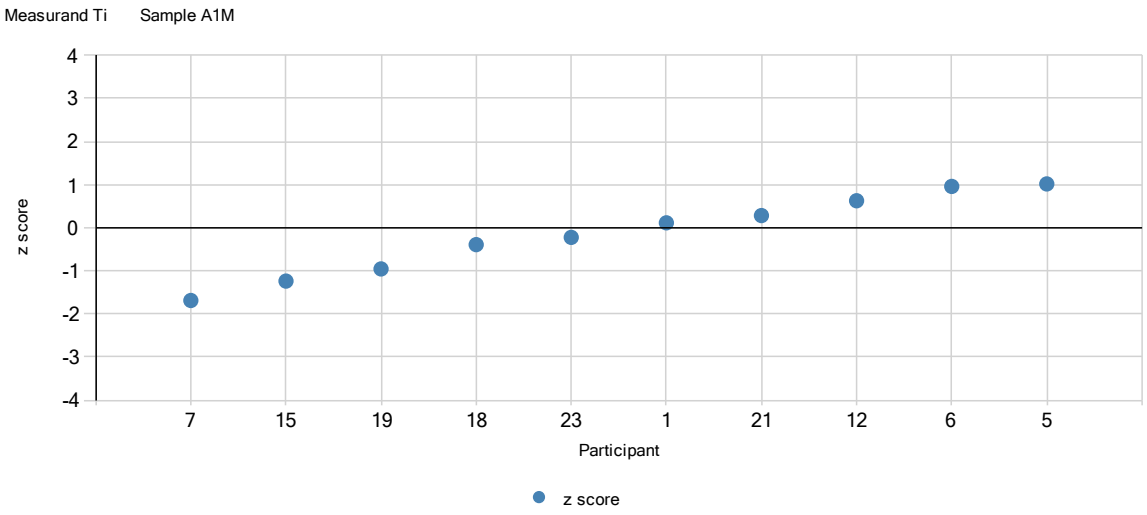


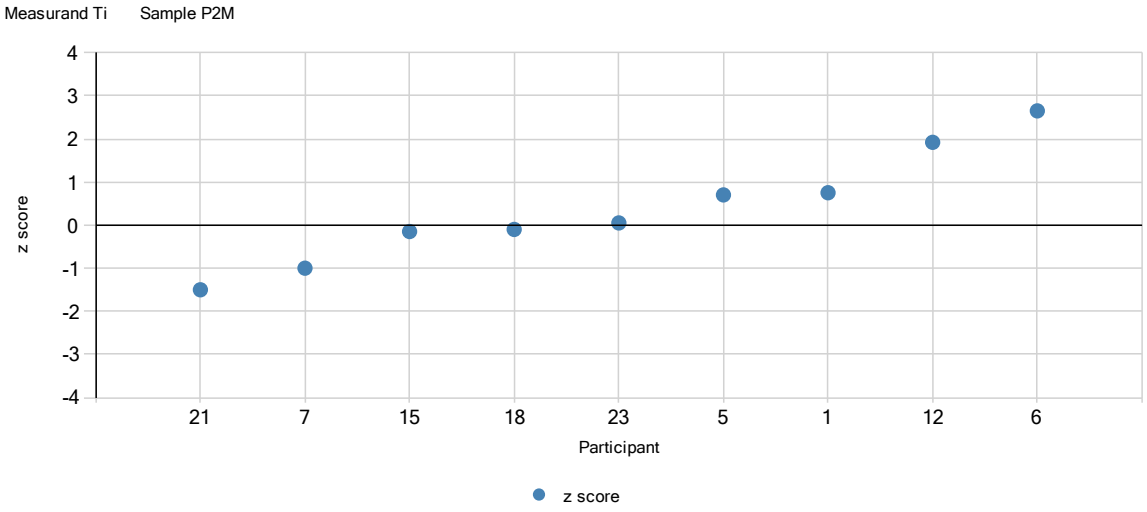
Measurand Sr Sample TN3

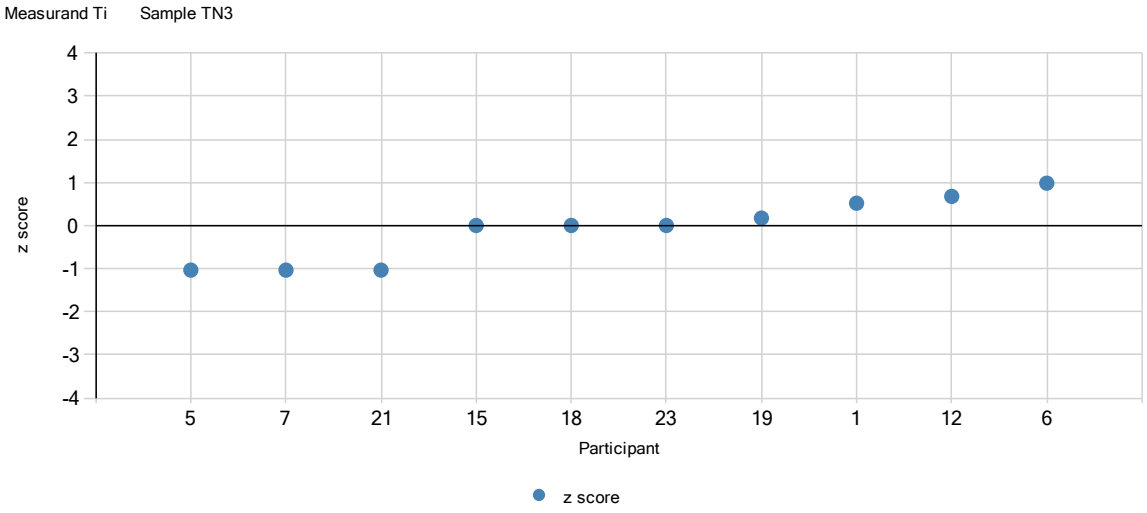


Measurand Sr Sample V4M

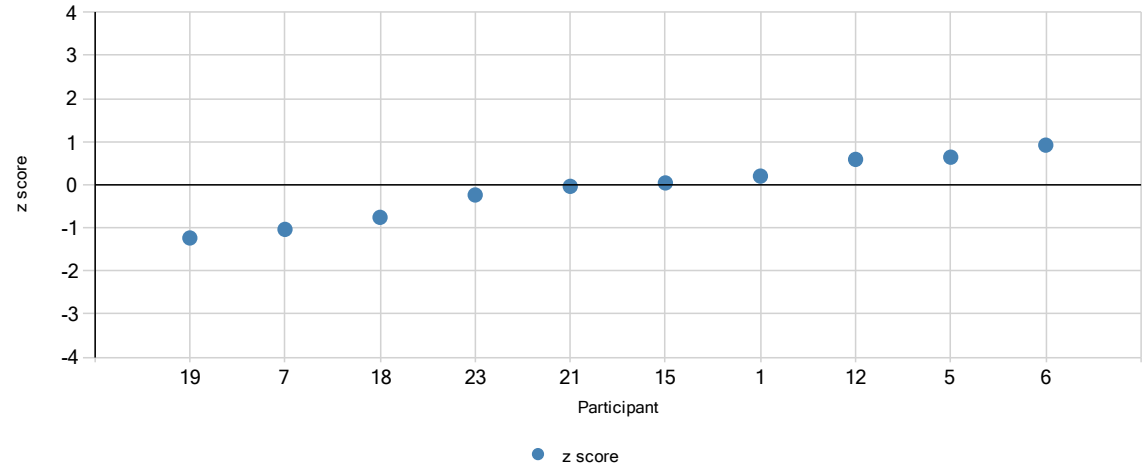



Measurand Ti
Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
7
15
19
18
23
1
21
12
6
5
Participant
z score

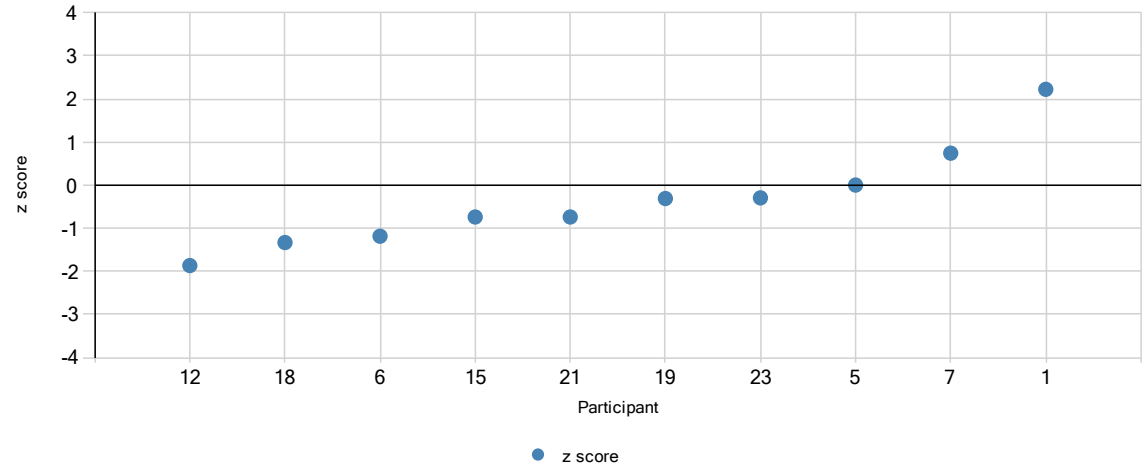

Measurand Ti
Sample P2M
z score
4
3
2
1
0
-1
-2
-3
-4
21
7
15
18
23
5
1
12
6
Participant
z score


Measurand Ti
Sample TN3
z score
4
3
2
1
0
-1
-2
-3
-4
5
7
21
15
18
23
19
1
12
6
Participant
z score

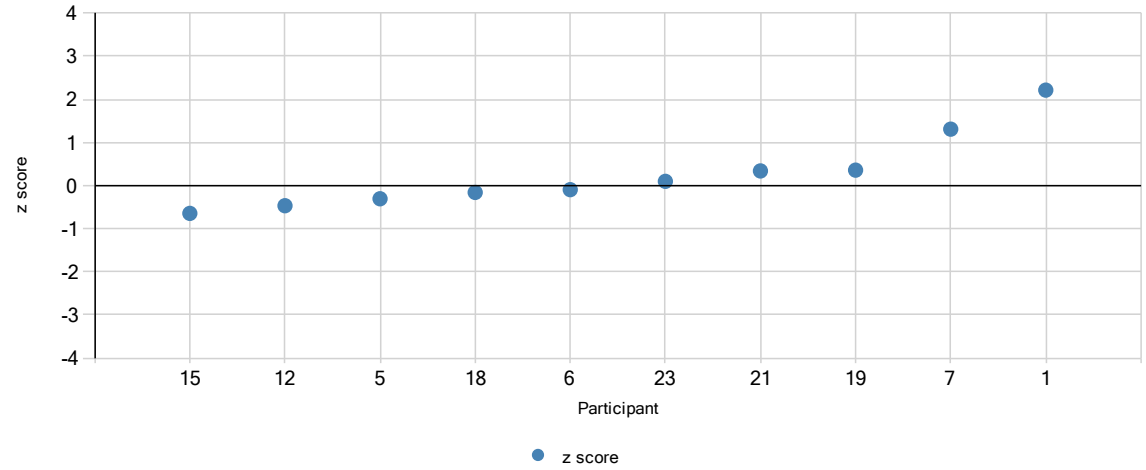
Measurand Ti Sample V4M



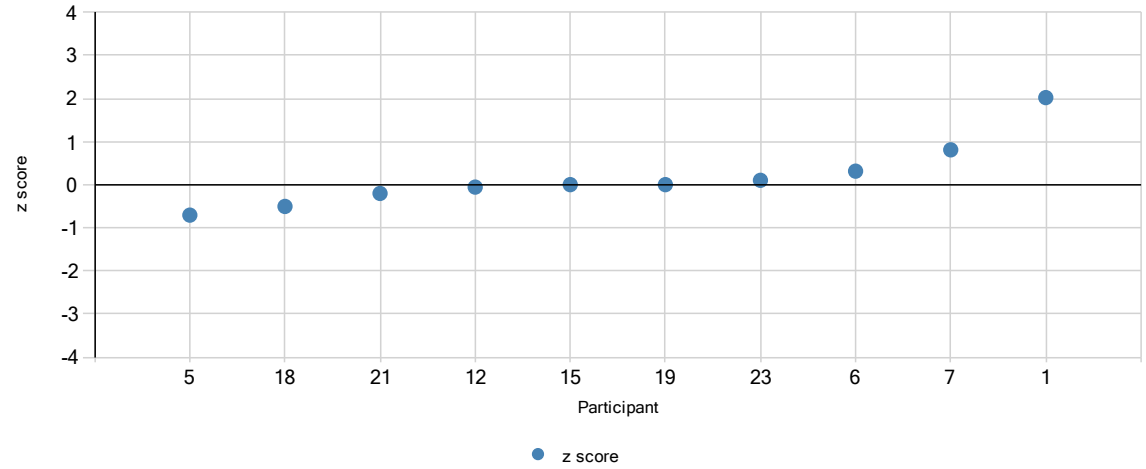
Measurand V Sample A1M



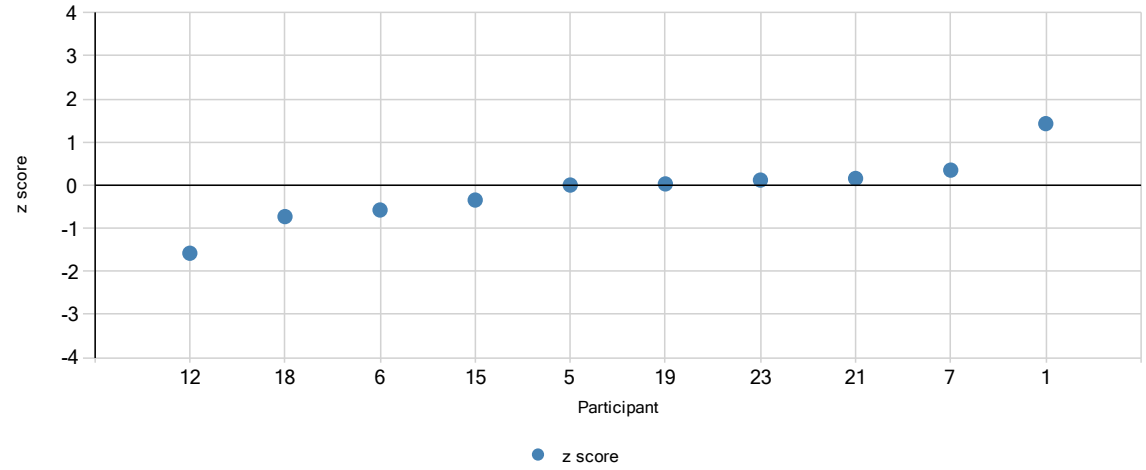
Measurand V Sample P2M



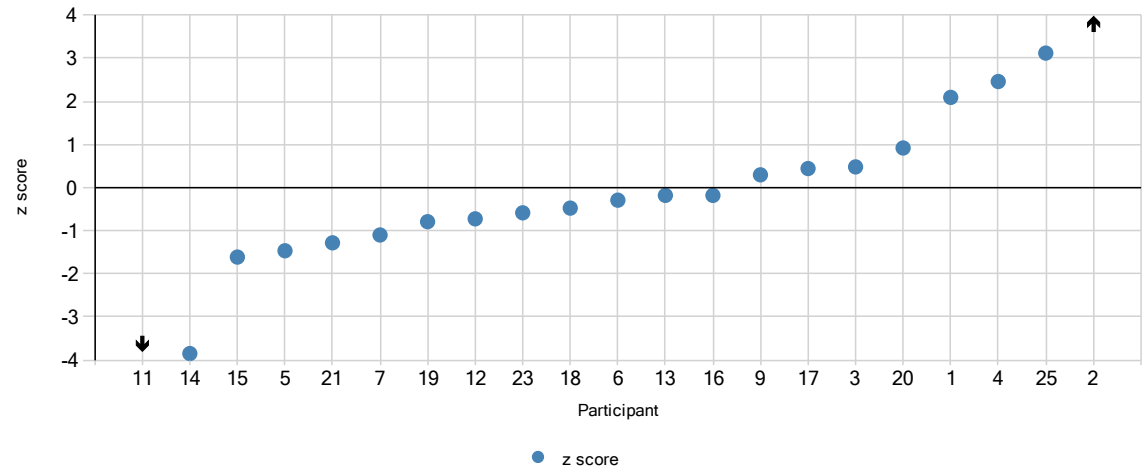
Measurand V Sample TN3



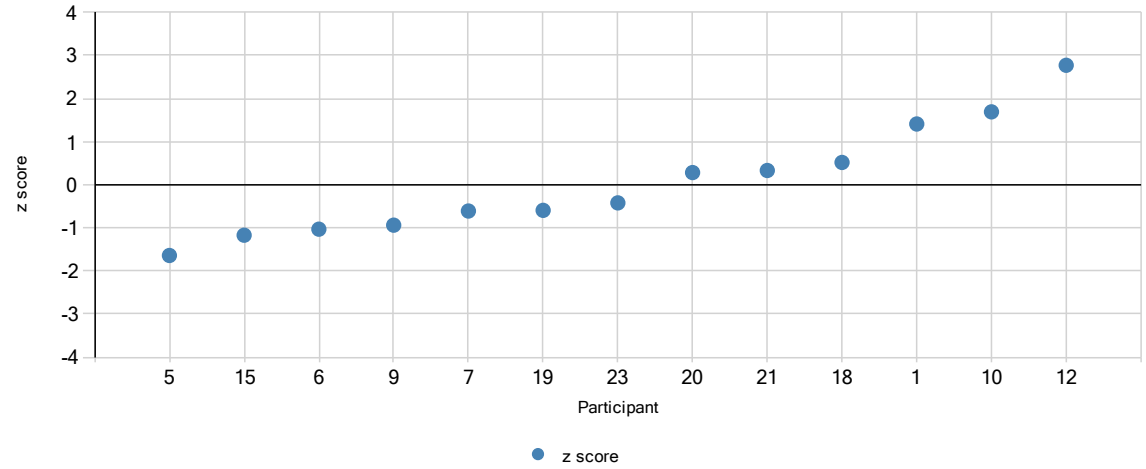
Measurand V Sample V4M



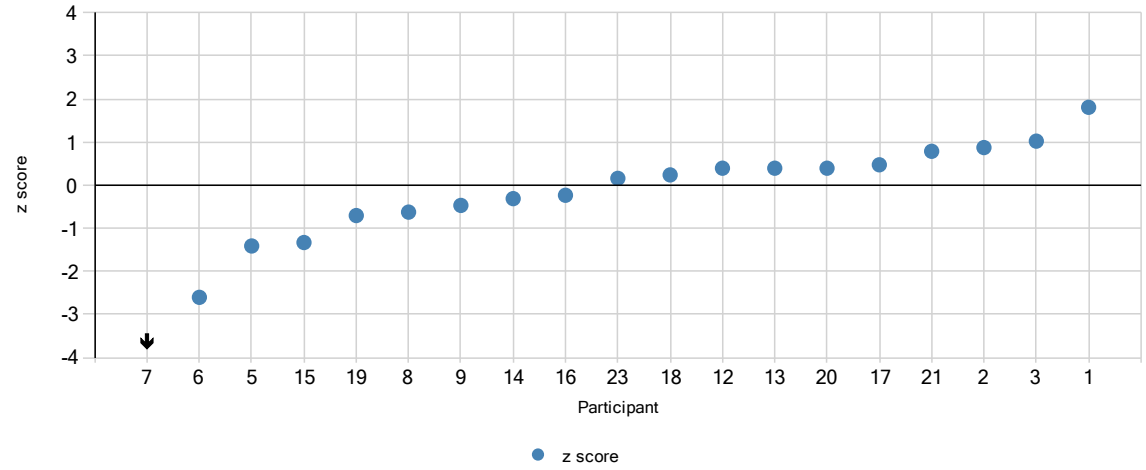
Measurand Zn Sample A1M



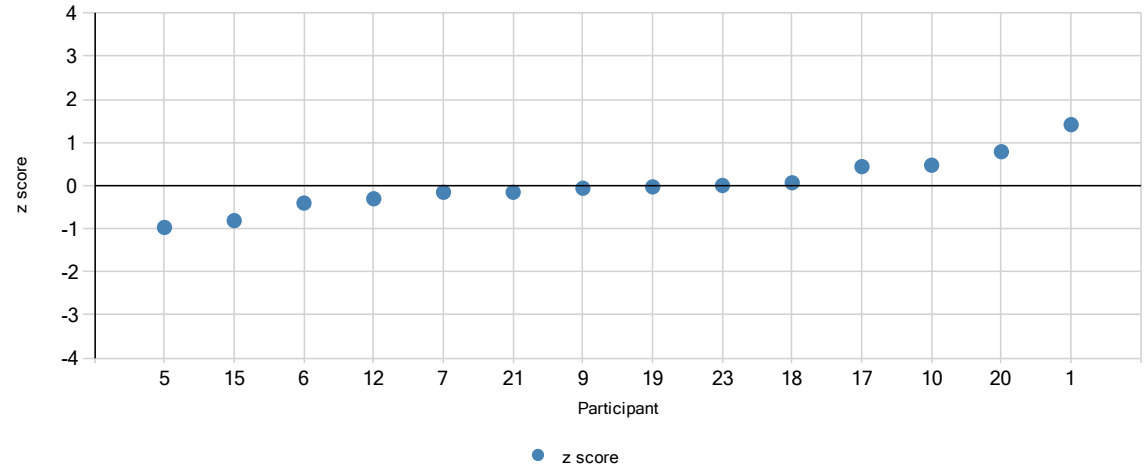
Measurand Zn Sample P2M



Measurand Zn Sample TN3



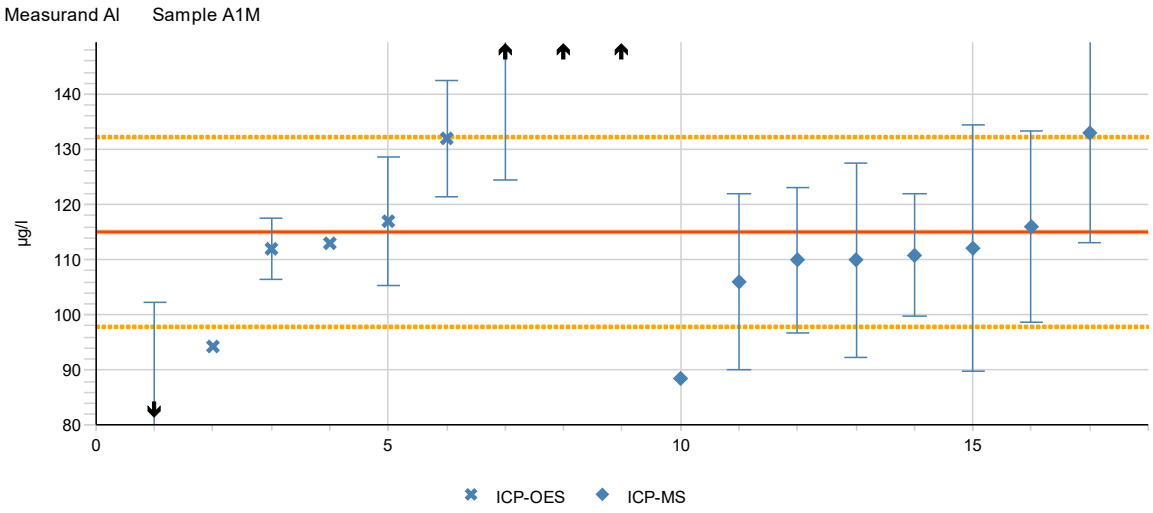
Measurand Zn Sample V4M

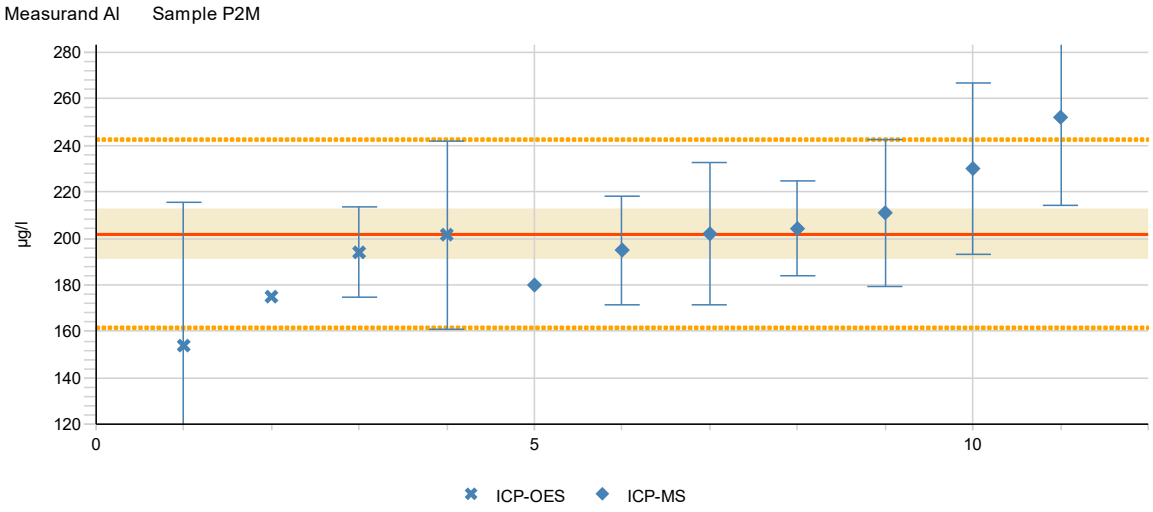


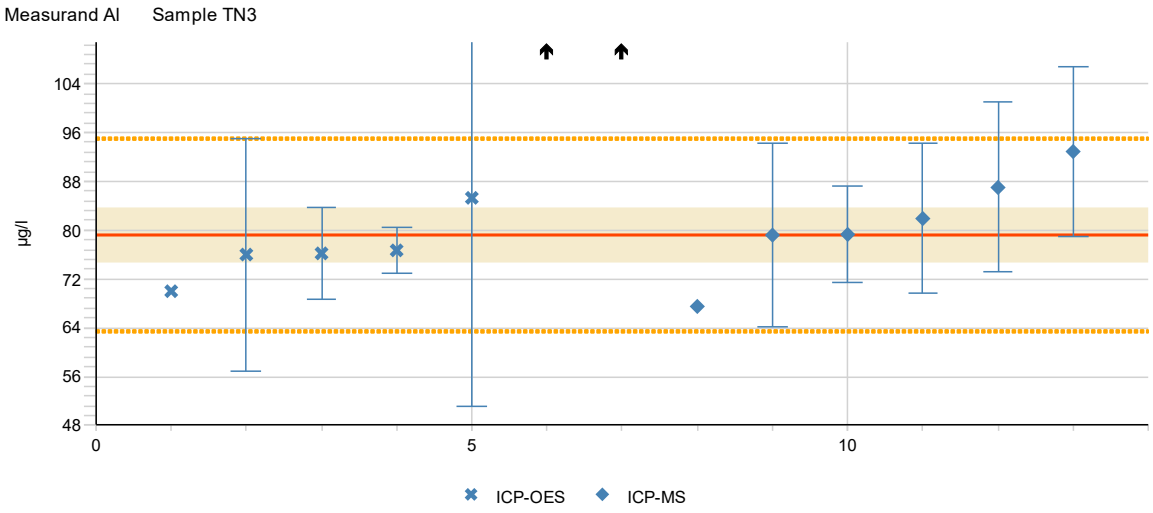
APPENDIX 11: Results grouped according to the methods

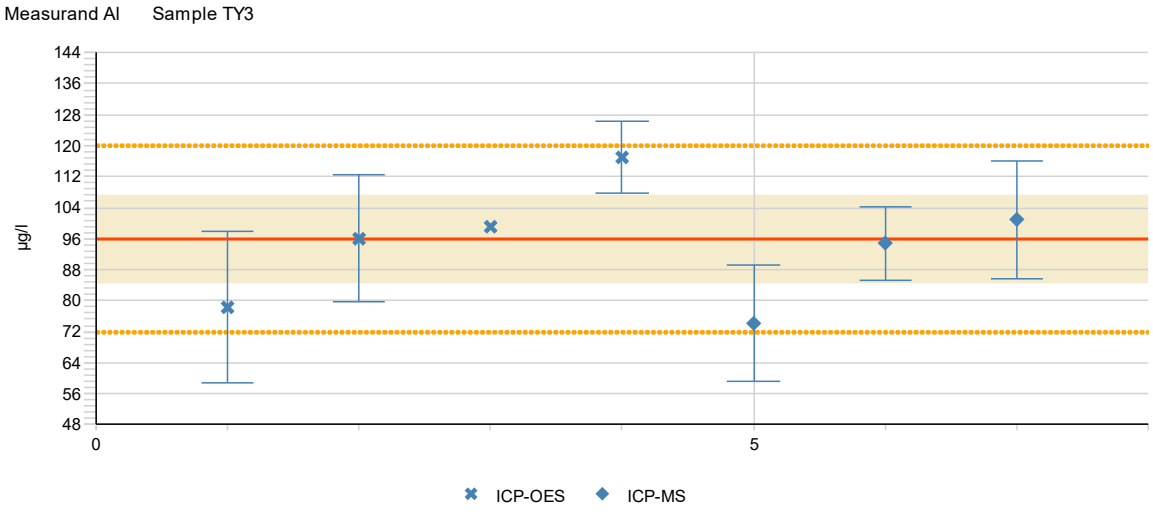
In figures:

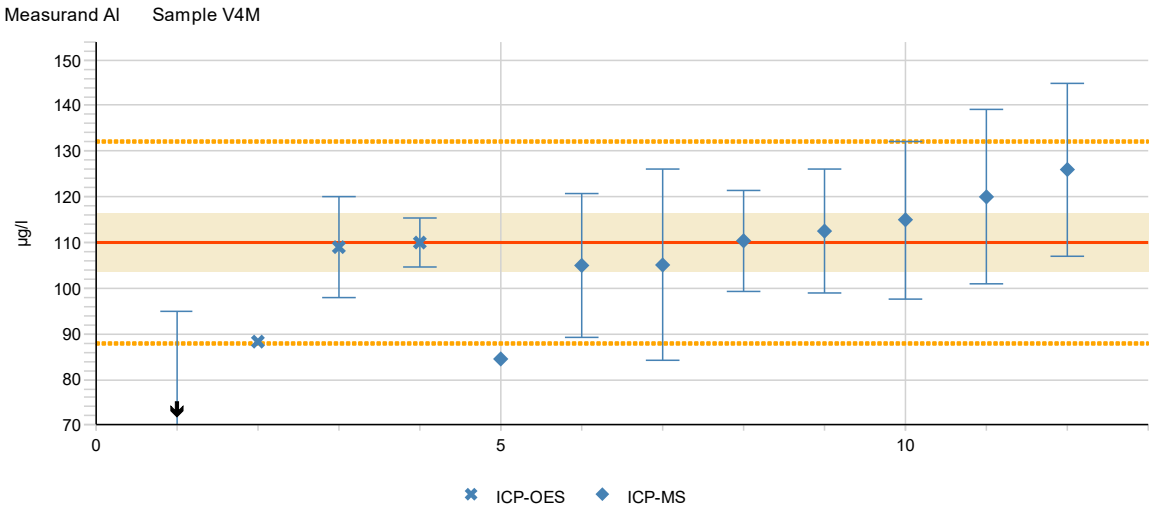
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded uncertainty of the assigned value, and the arrow describes the value outside the scale.

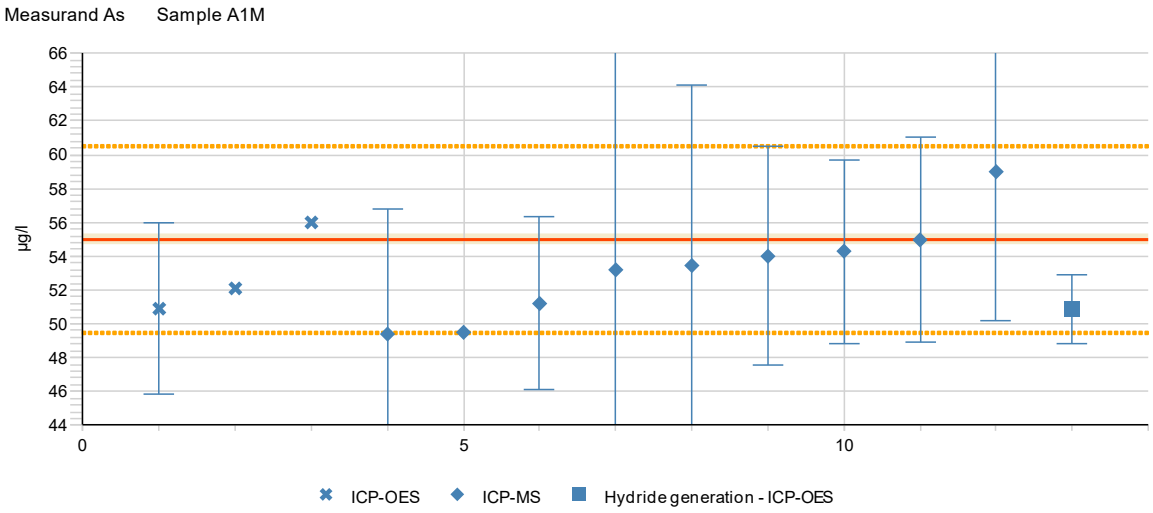


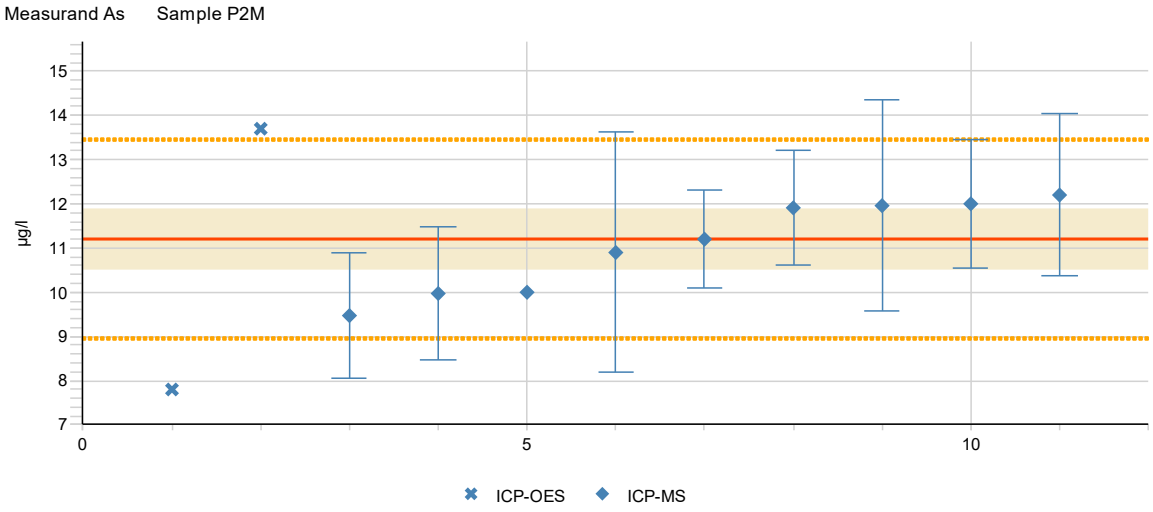


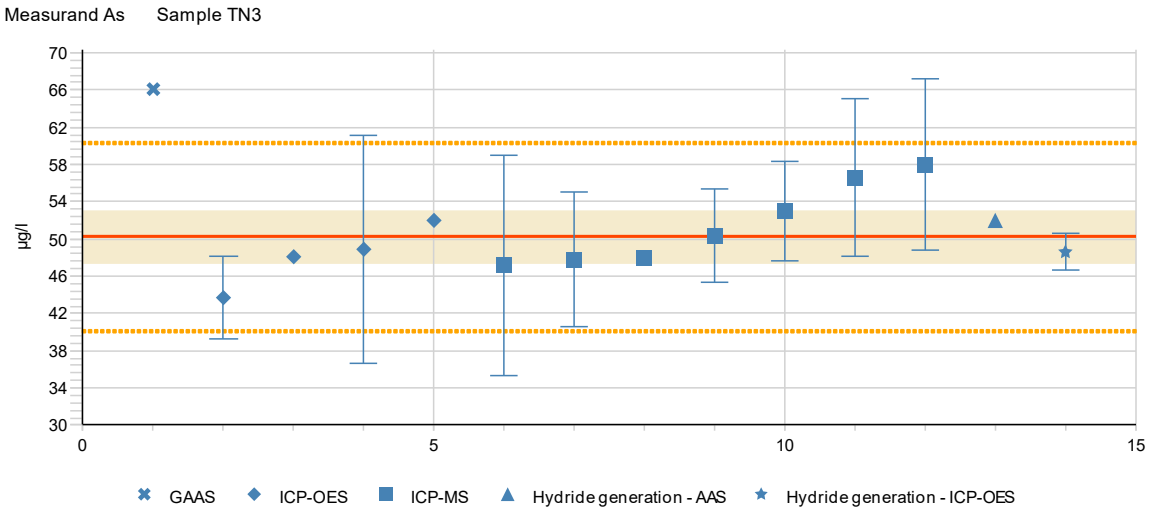

Measurand Al
Sample TN3
µg/l
104
96
88
80
72
64
56
48
0
5
10
ICP-OES
ICP-MS


Measurand Al
Sample TY3
µg/l
144
136
128
120
112
104
96
88
80
72
64
56
48
0
5
ICP-OES
ICP-MS

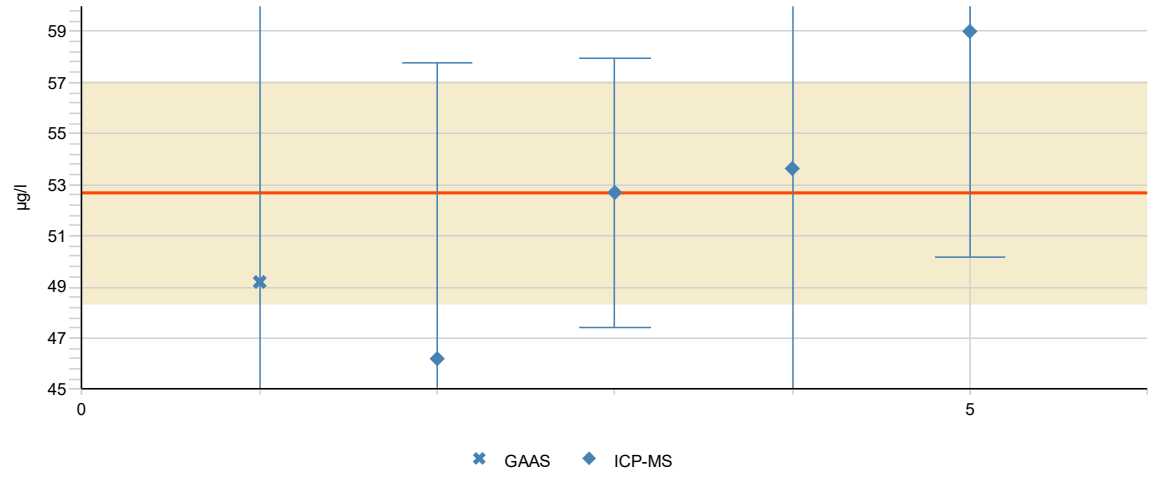

Measurand Al
Sample V4M
µg/l
150
140
130
120
110
100
90
80
70
0
5
10
ICP-OES
ICP-MS


Measurand As Sample A1M
µg/l
66
64
62
60
58
56
54
52
50
48
46
44
0
5
10
ICP-OES
ICP-MS
Hydride generation - ICP-OES

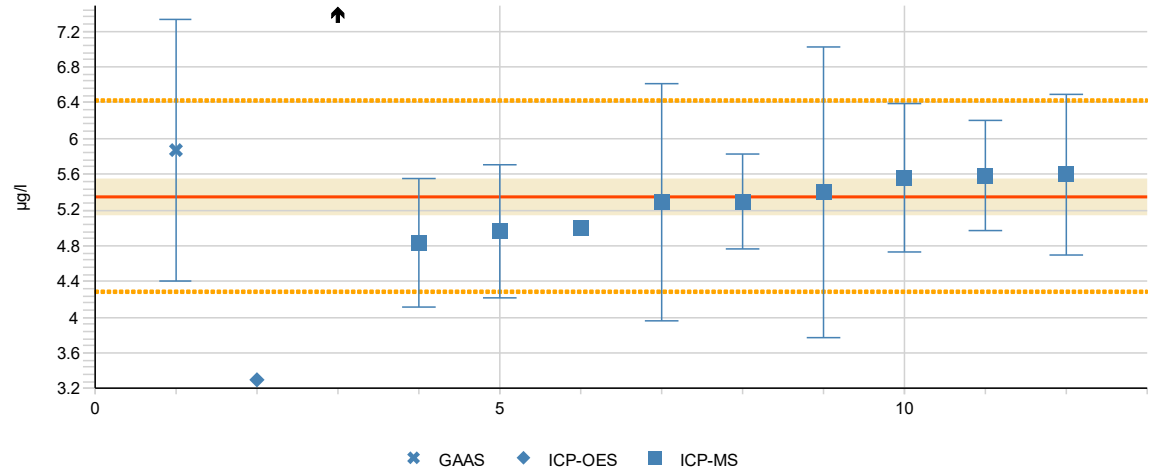

Measurand As Sample P2M
µg/l
15
14
13
12
11
10
9
8
7
0
5
10
ICP-OES
ICP-MS


Measurand As Sample TN3
µg/l
70
66
62
58
54
50
46
42
38
34
30
0
5
10
15
GAAS
ICP-OES
ICP-MS
Hydride generation - AAS
Hydride generation - ICP-OES

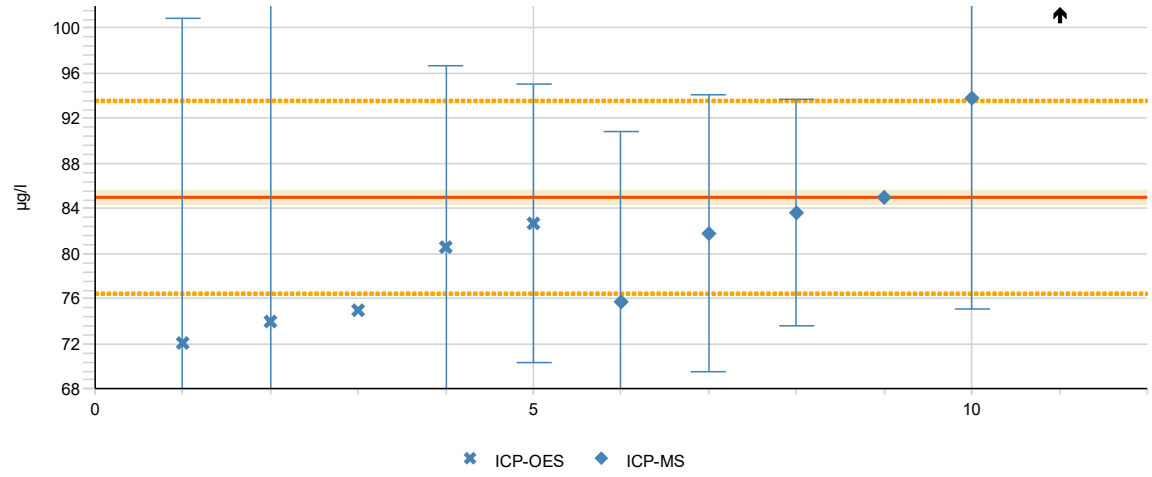
Measurand As Sample TY3

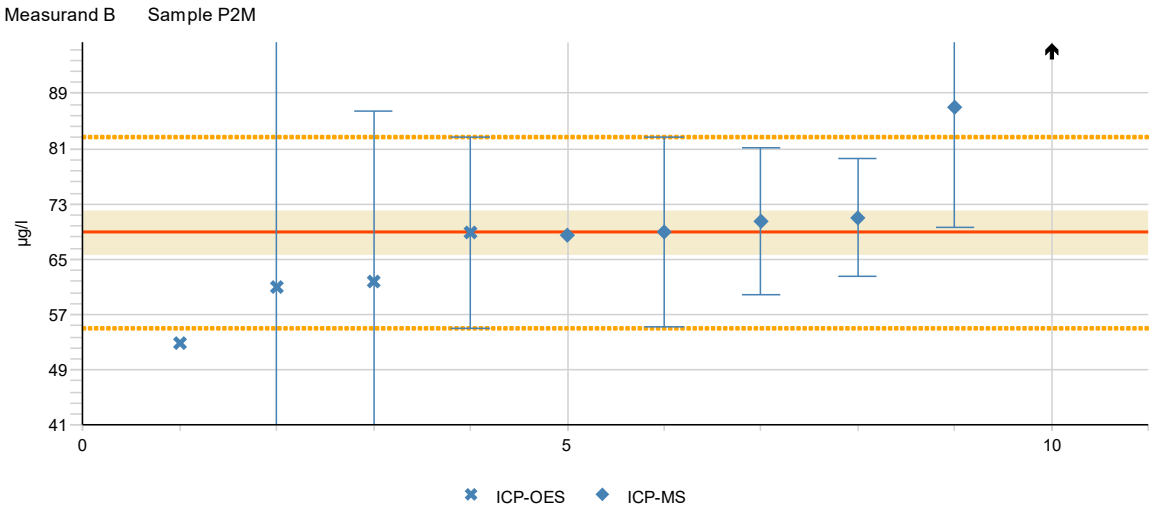


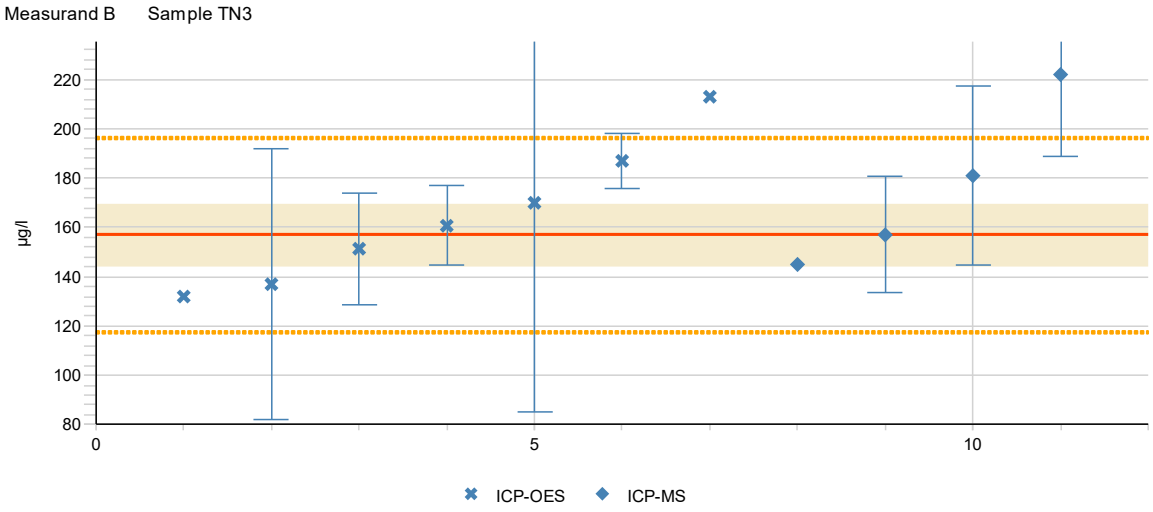
Measurand As Sample V4M

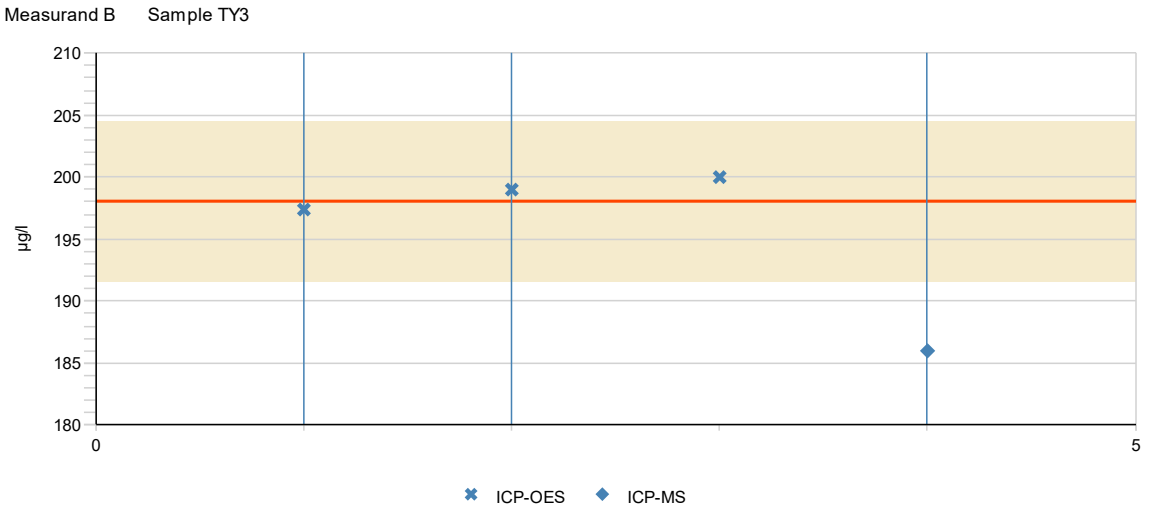


Measurand B Sample A1M

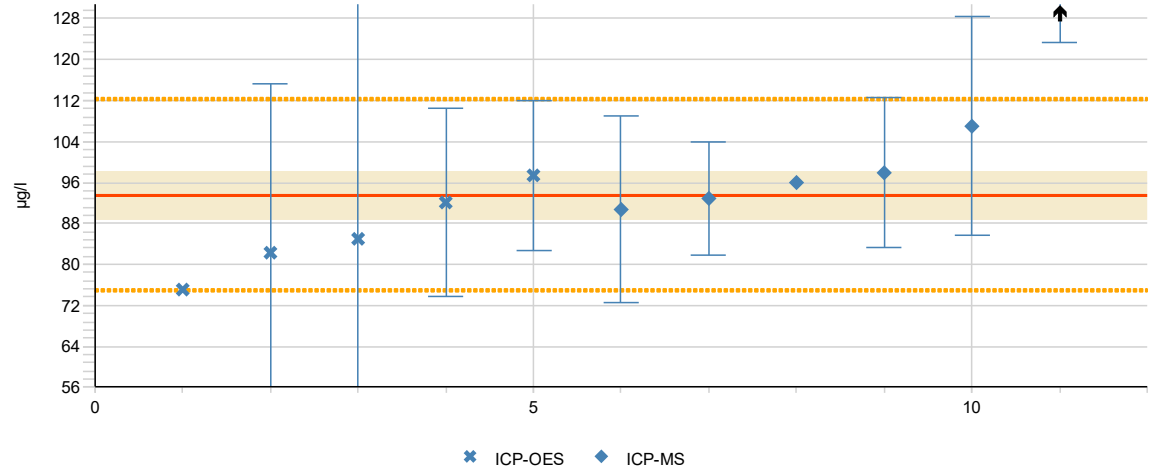



Measurand B Sample P2M
µg/l
89
81
73
65
57
49
41
0
5
10
ICP-OES
ICP-MS

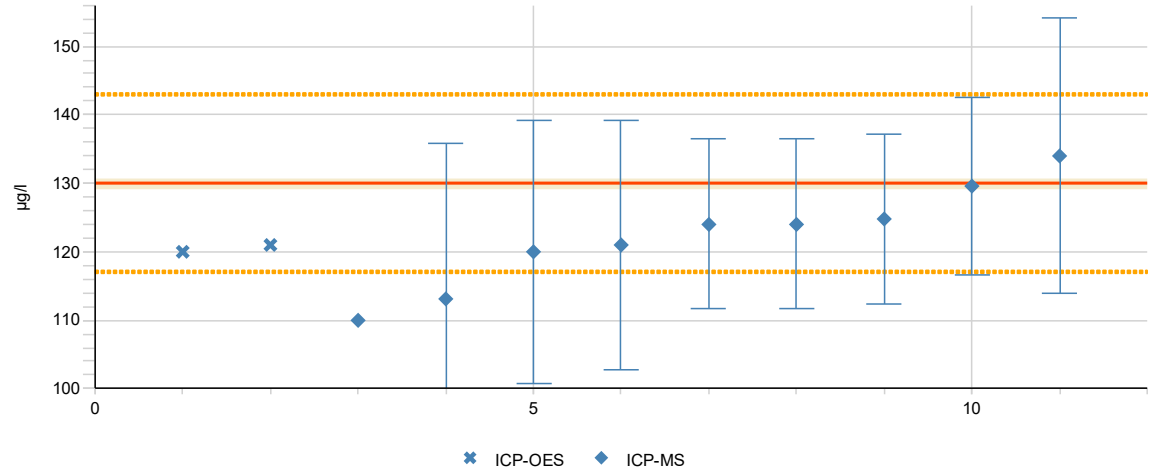

Measurand B Sample TN3
µg/l
220
200
180
160
140
120
100
80
0
5
10
ICP-OES
ICP-MS


Measurand B Sample TY3
µg/l
210
205
200
195
190
185
180
0
5
ICP-OES
ICP-MS

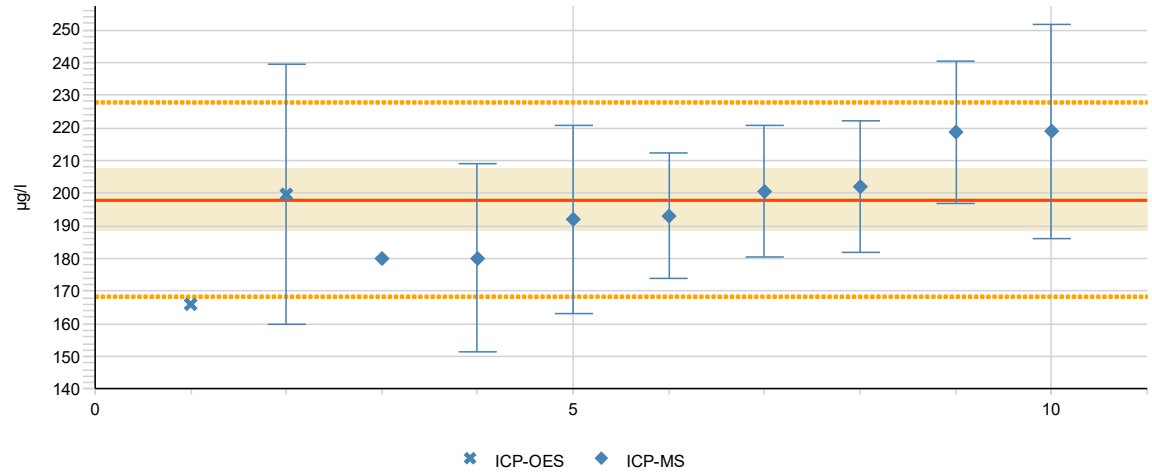
Measurand B Sample V4M

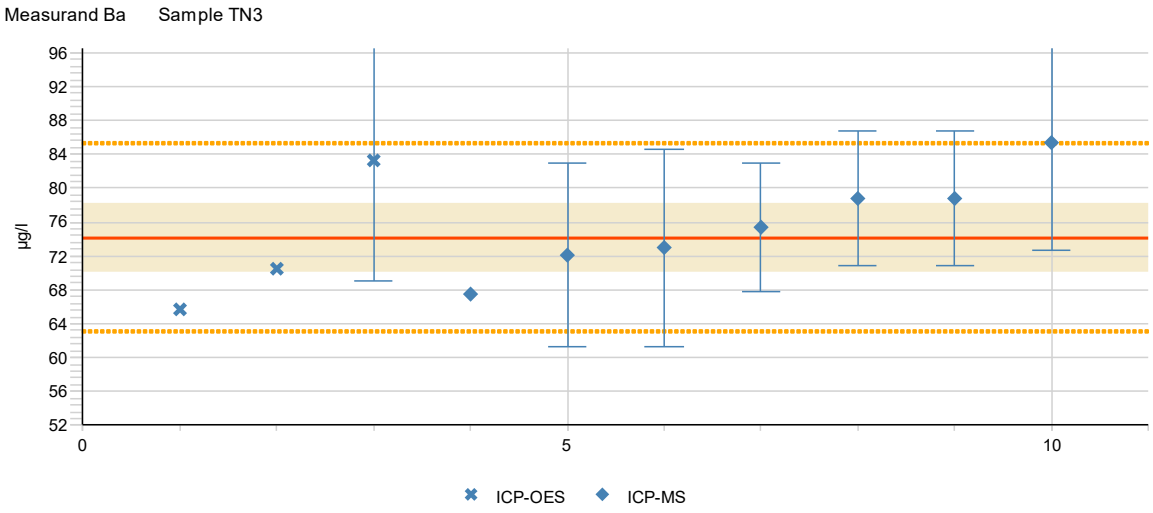


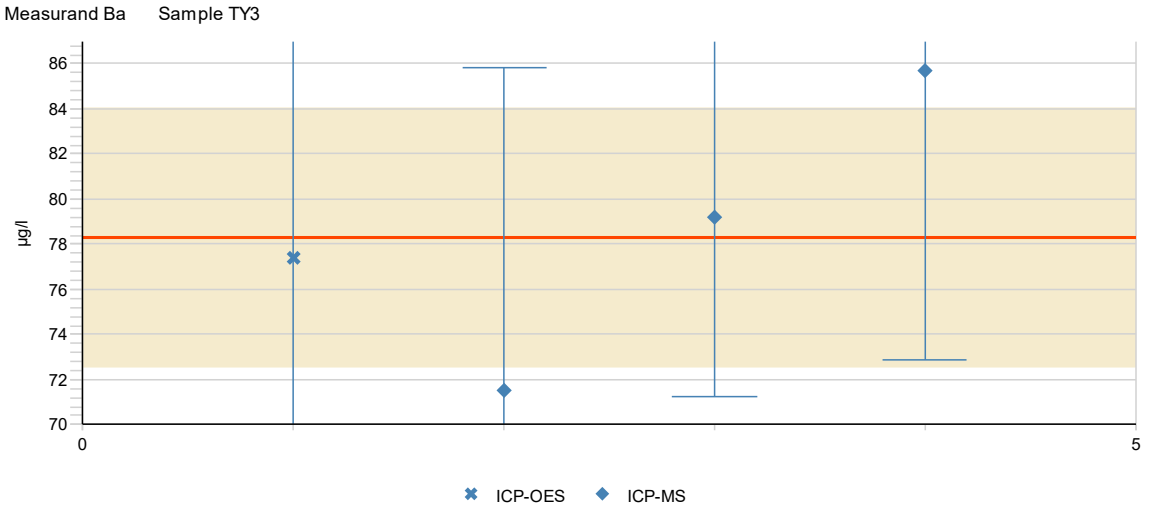
Measurand Ba Sample A1M

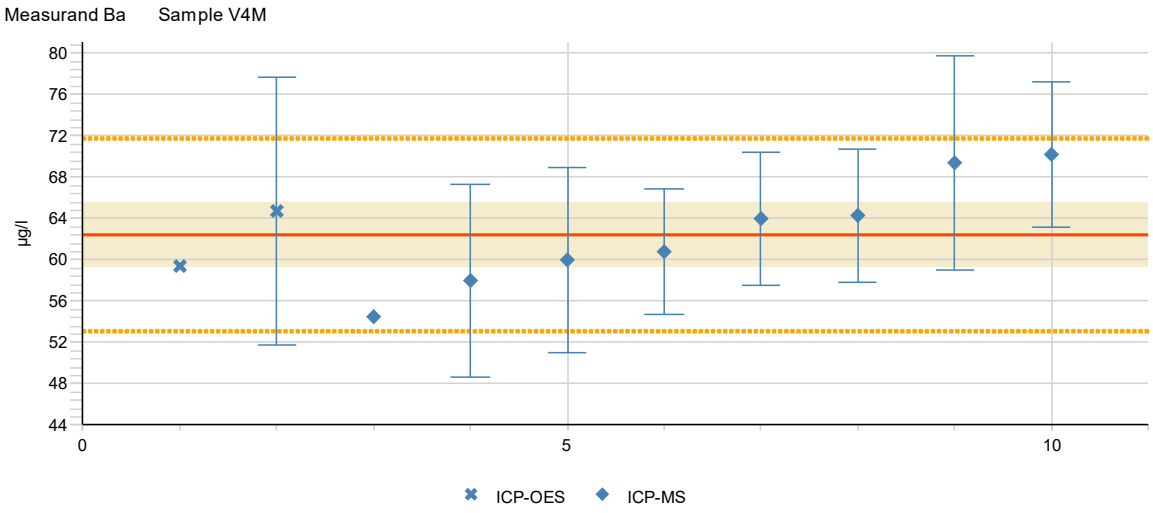


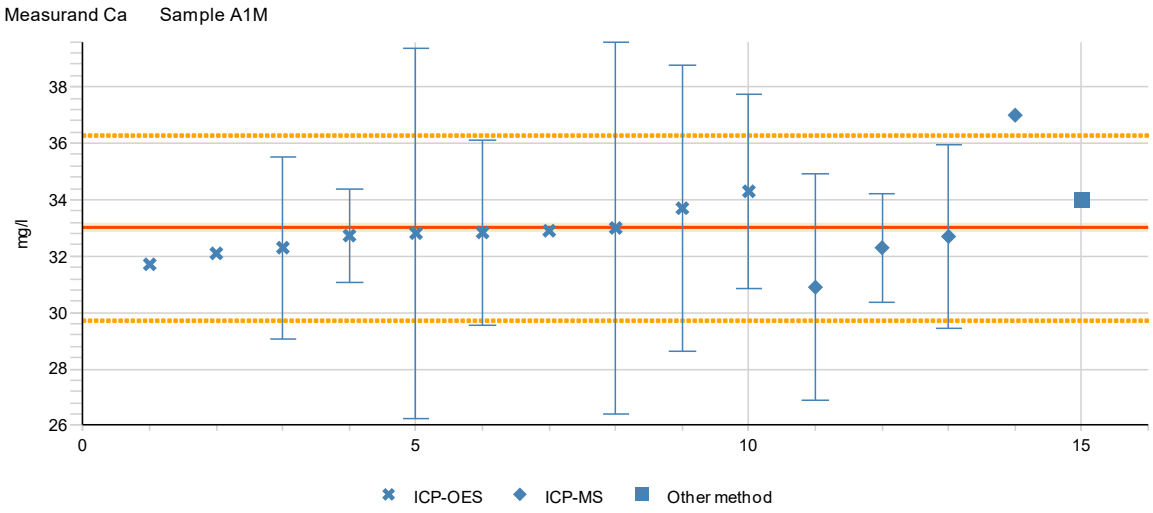
Measurand Ba Sample P2M

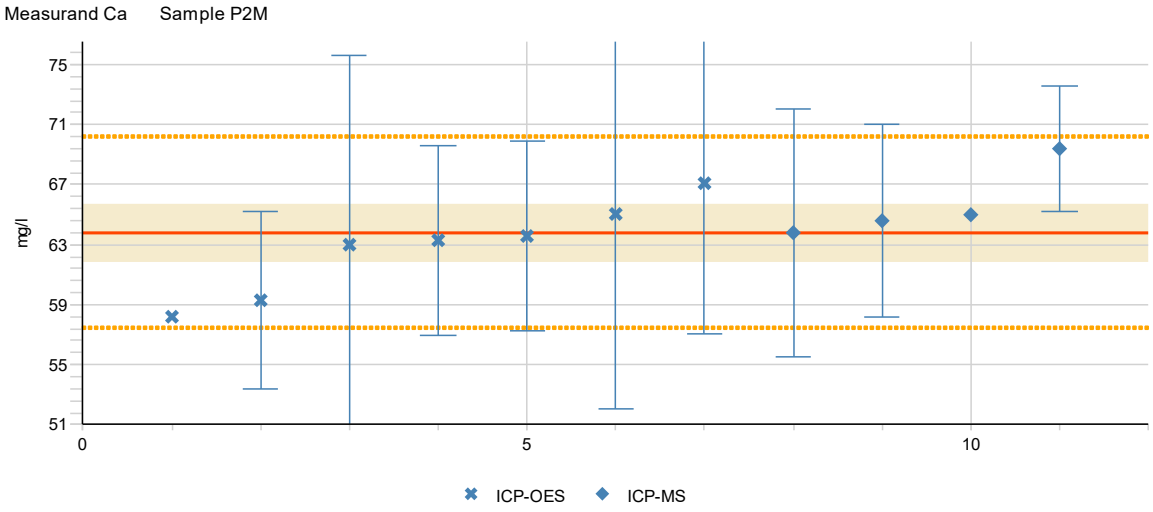


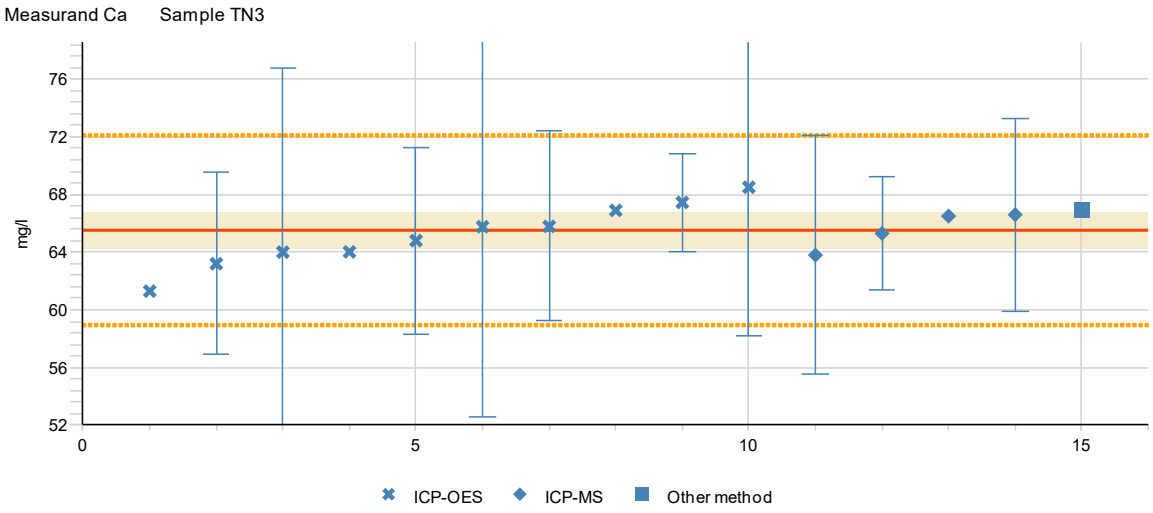

Measurand Ba Sample TN3
96
92
88
84
80
76
72
68
64
60
56
52
µg/l
0
5
10
ICP-OES
ICP-MS

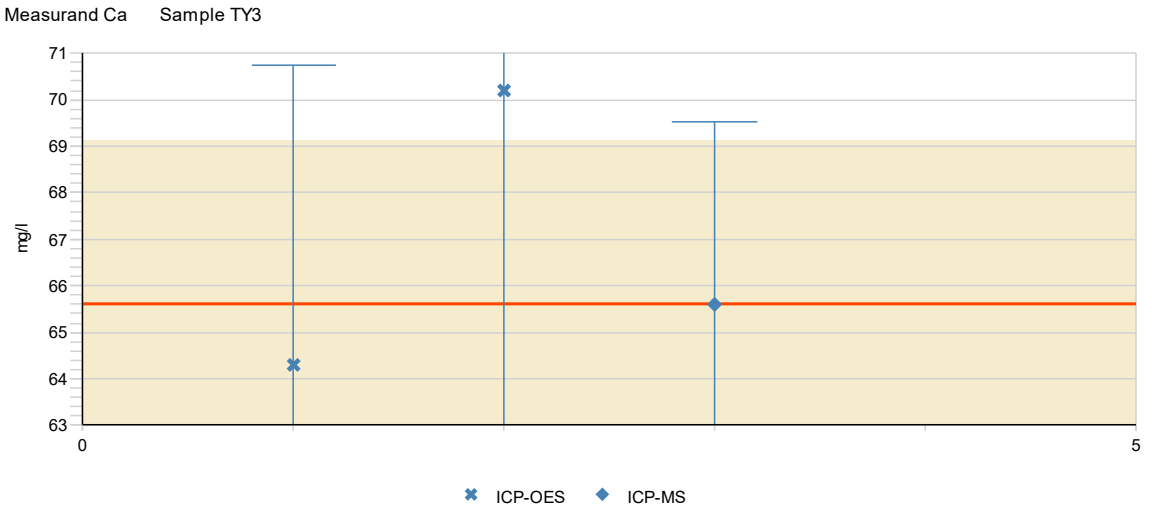

Measurand Ba Sample TY3
86
84
82
80
78
76
74
72
70
µg/l
0
5
ICP-OES
ICP-MS

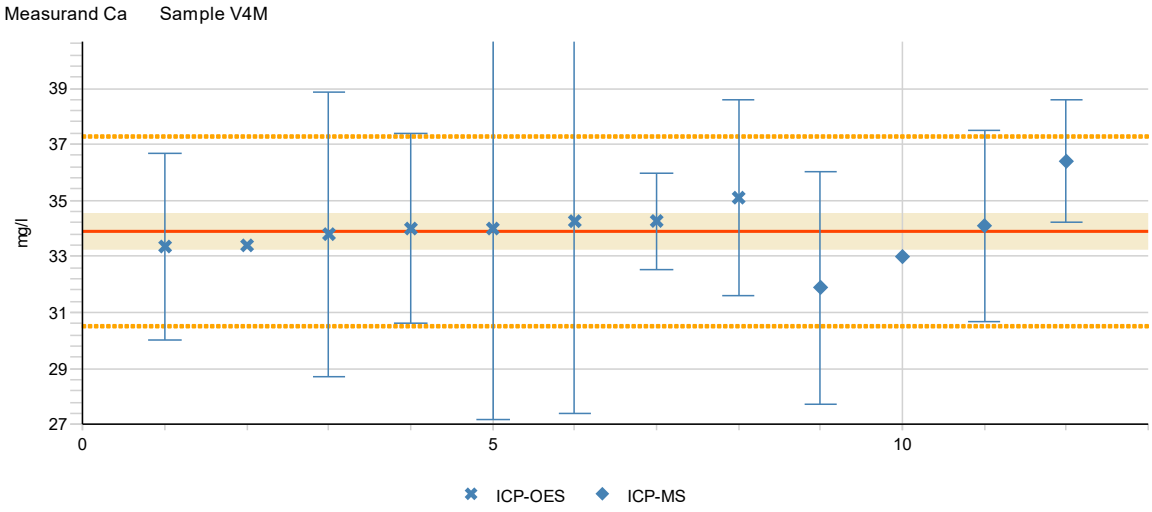

Measurand Ba Sample V4M
80
76
72
68
64
60
56
52
48
44
µg/l
0
5
10
ICP-OES
ICP-MS

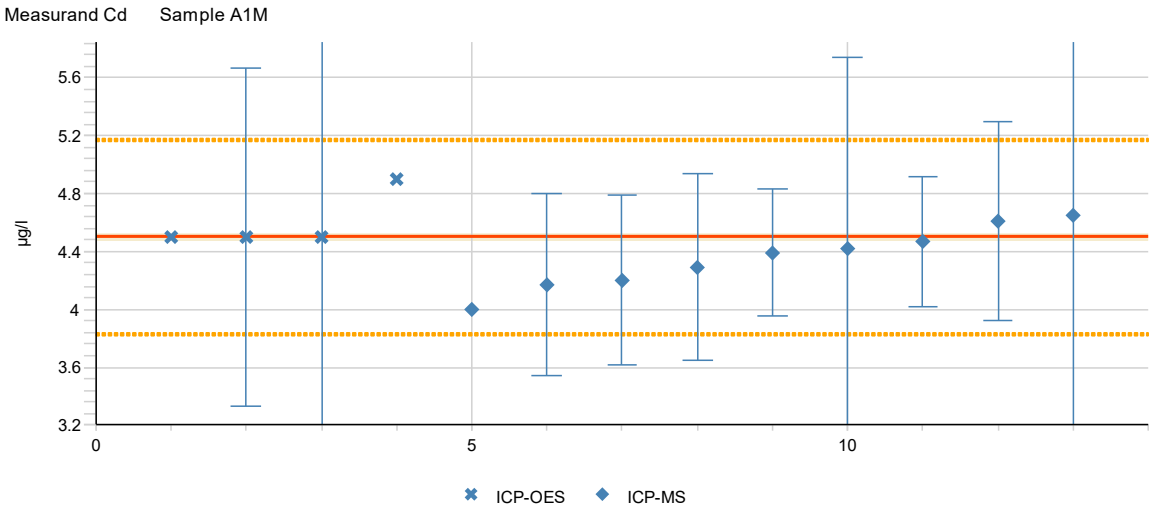

Measurand Ca Sample A1M
mg/l
38
36
34
32
30
28
26
0
5
10
15
ICP-OES
ICP-MS
Other method


Measurand Ca Sample P2M
mg/l
75
71
67
63
59
55
51
0
5
10
ICP-OES
ICP-MS

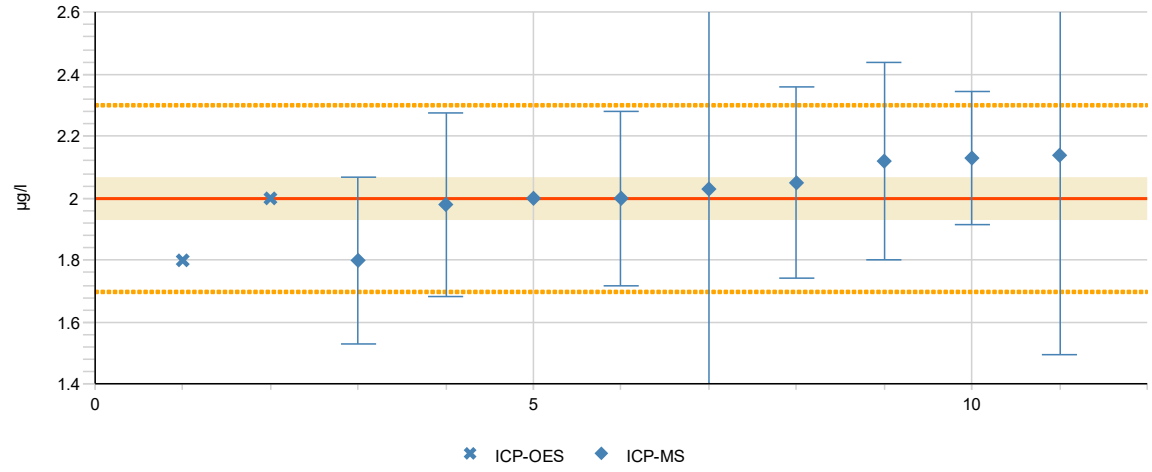

Measurand Ca Sample TN3
mg/l
76
72
68
64
60
56
52
0
5
10
15
ICP-OES
ICP-MS
Other method


Measurand Ca Sample TY3
mg/l
71
70
69
68
67
66
65
64
63
0
5
ICP-OES
ICP-MS

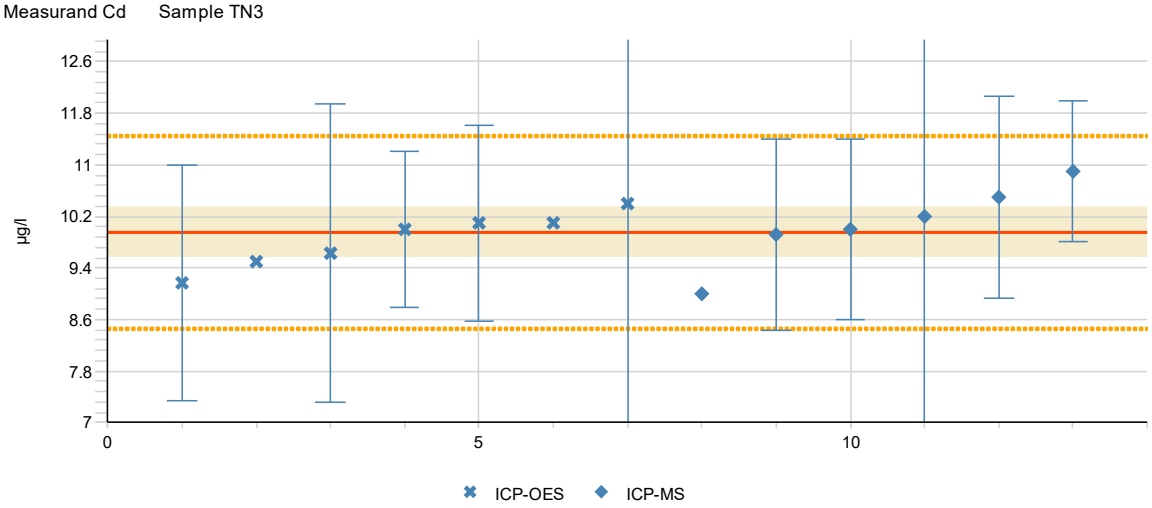

Measurand Ca Sample V4M
mg/l
39
37
35
33
31
29
27
0
5
10
ICP-OES
ICP-MS


Measurand Cd Sample A1M
µg/l
5.6
5.2
4.8
4.4
4
3.6
3.2
0
5
10
ICP-OES
ICP-MS

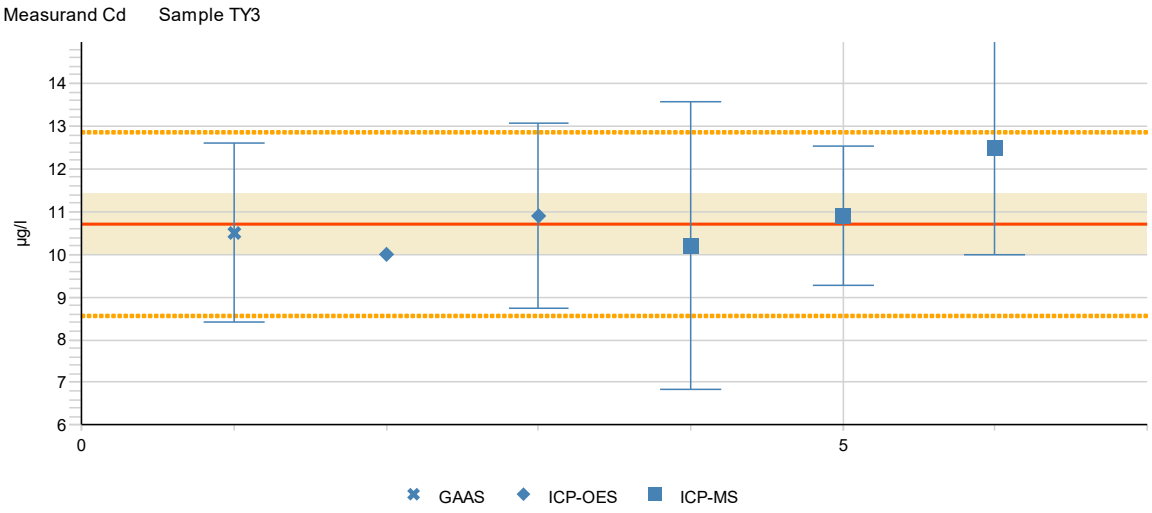
Measurand Cd Sample P2M

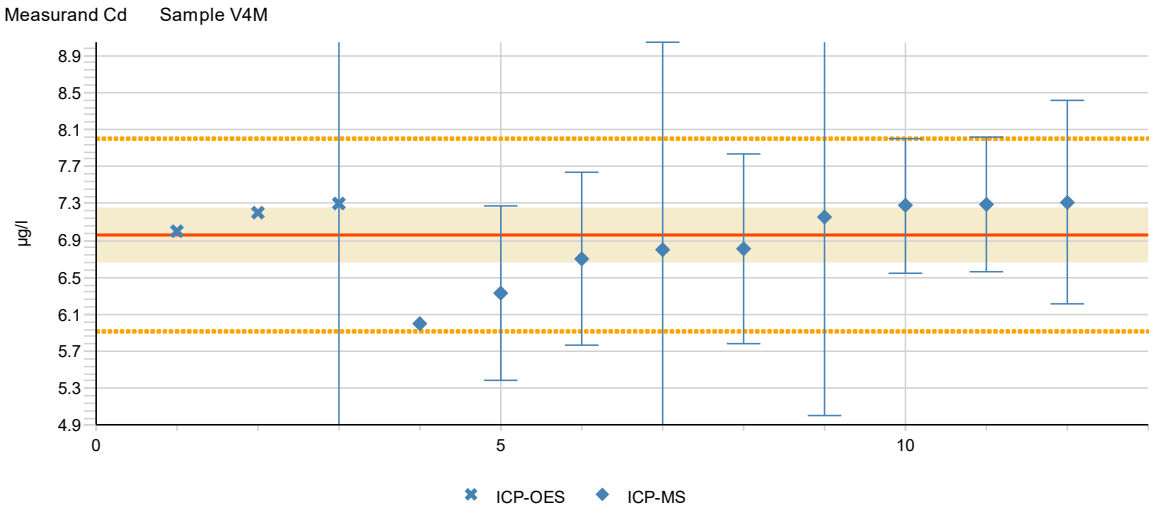


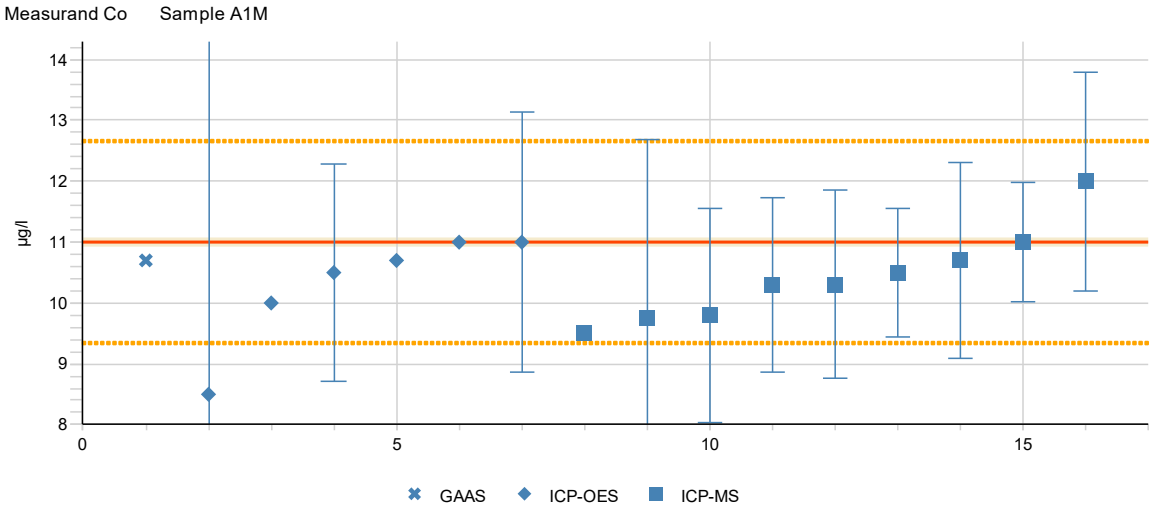
Measurand Cd Sample TN3

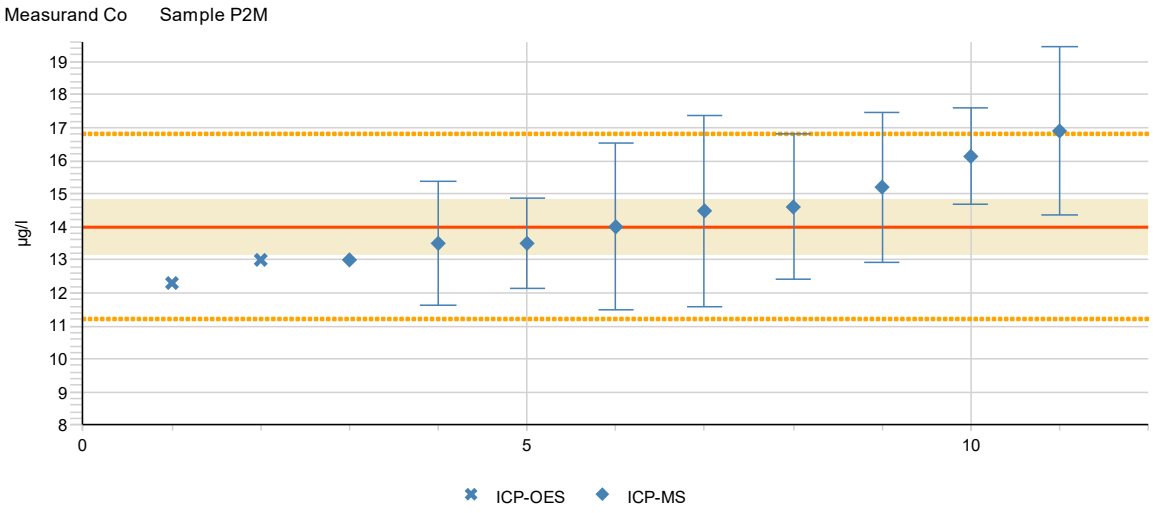


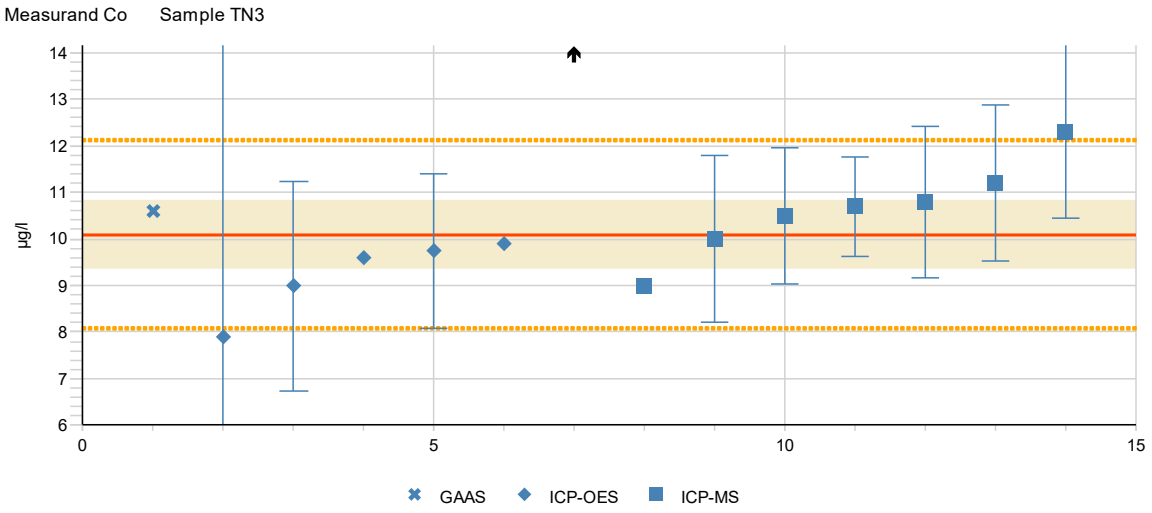
Measurand Cd Sample TY3

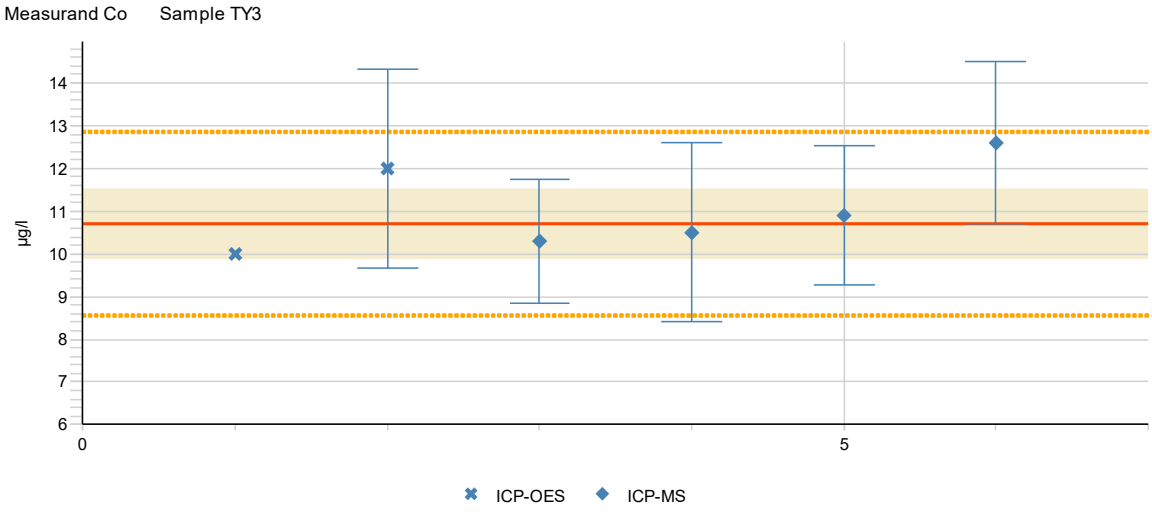


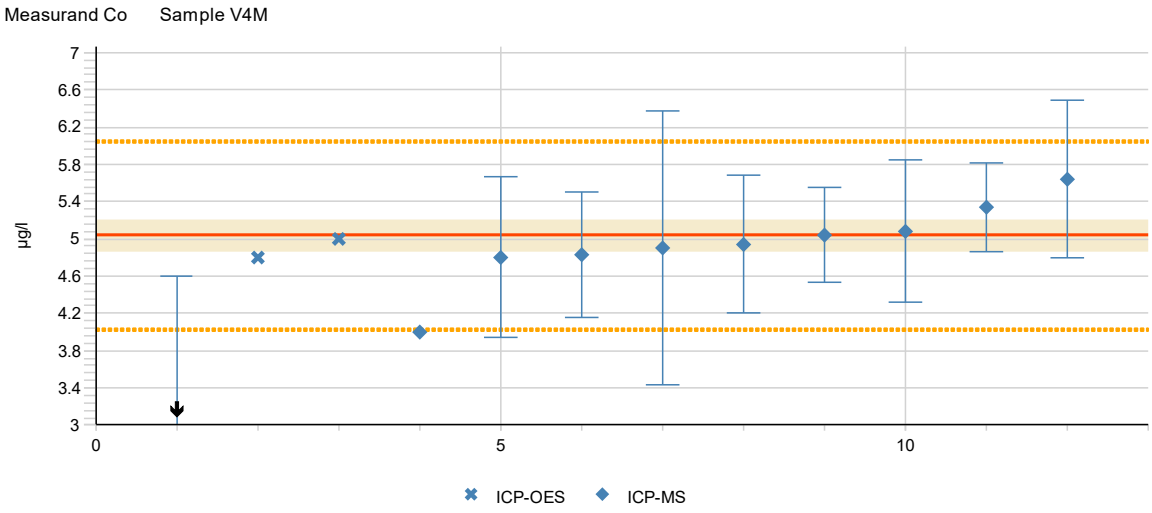

Measurand Cd Sample V4M
µg/l
8.9
8.5
8.1
7.7
7.3
6.9
6.5
6.1
5.7
5.3
4.9
0
5
10
ICP-OES
ICP-MS

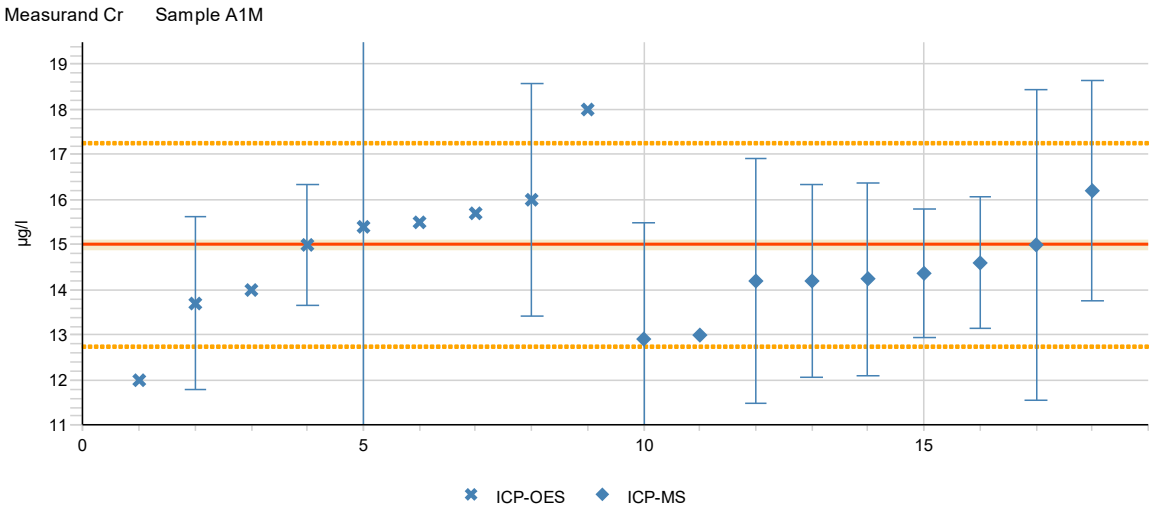

Measurand Co Sample A1M
µg/l
14
13
12
11
10
9
8
0
5
10
15
GAAS
ICP-OES
ICP-MS

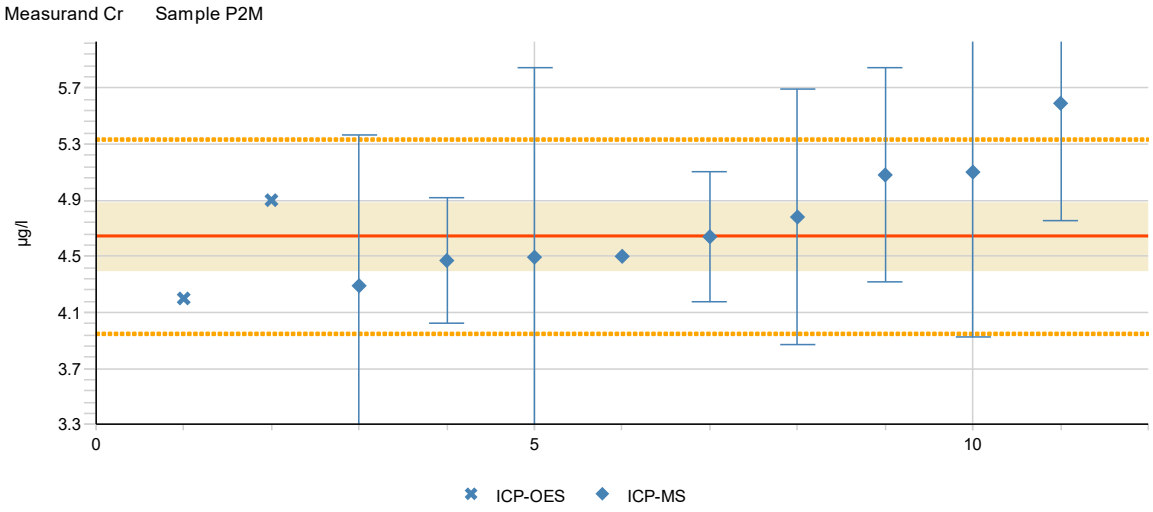

Measurand Co Sample P2M
µg/l
19
18
17
16
15
14
13
12
11
10
9
8
0
5
10
ICP-OES
ICP-MS

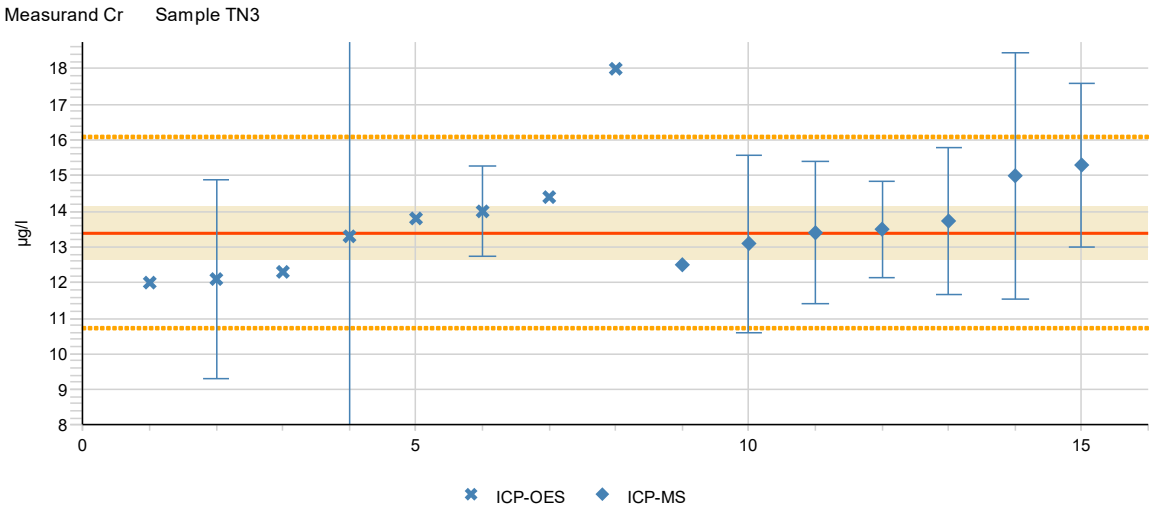

Measurand Co
Sample TN3
µg/l
14
13
12
11
10
9
8
7
6
0
5
10
15
GAAS
ICP-OES
ICP-MS


Measurand Co
Sample TY3
µg/l
14
13
12
11
10
9
8
7
6
0
5
ICP-OES
ICP-MS

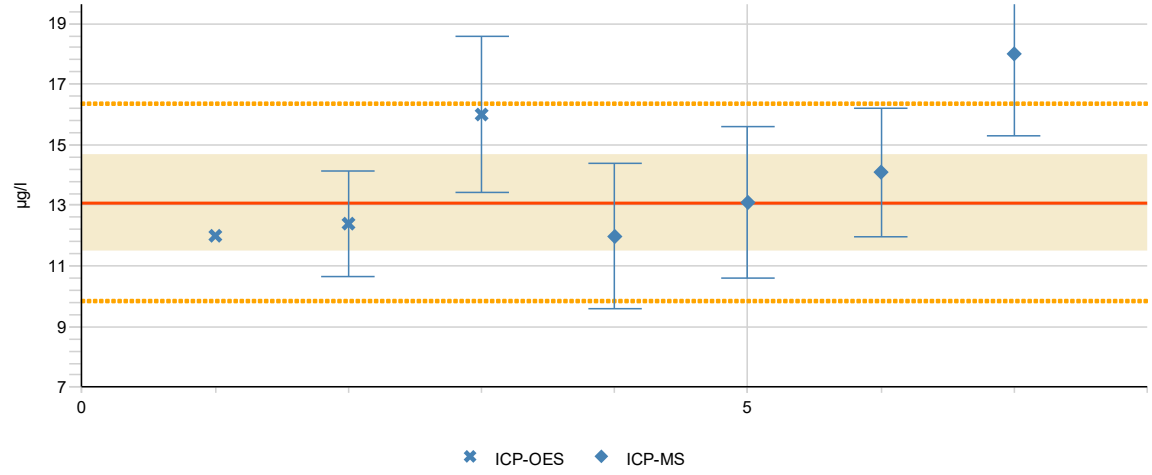

Measurand Co
Sample V4M
µg/l
7
6.6
6.2
5.8
5.4
5
4.6
4.2
3.8
3.4
3
0
5
10
ICP-OES
ICP-MS


Measurand Cr Sample A1M
µg/l
19
18
17
16
15
14
13
12
11
0
5
10
15
ICP-OES
ICP-MS

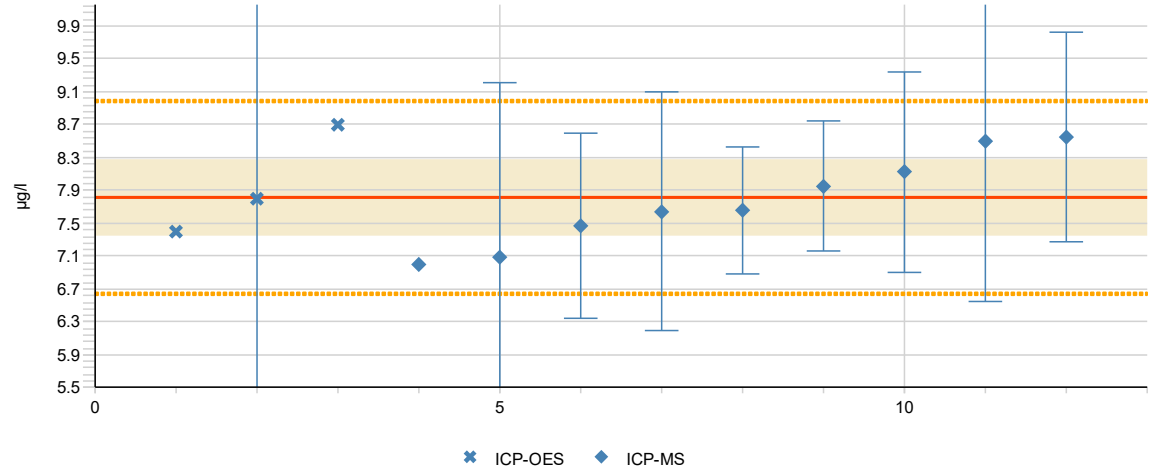

Measurand Cr Sample P2M
µg/l
5.7
5.3
4.9
4.5
4.1
3.7
3.3
0
5
10
ICP-OES
ICP-MS


Measurand Cr Sample TN3
µg/l
18
17
16
15
14
13
12
11
10
9
8
0
5
10
15
ICP-OES
ICP-MS

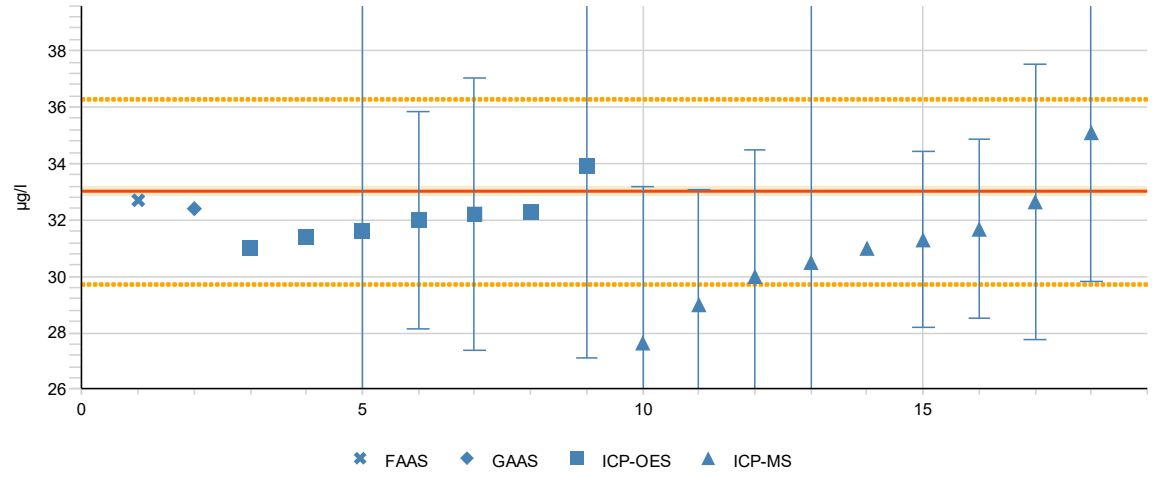
Measurand Cr Sample TY3

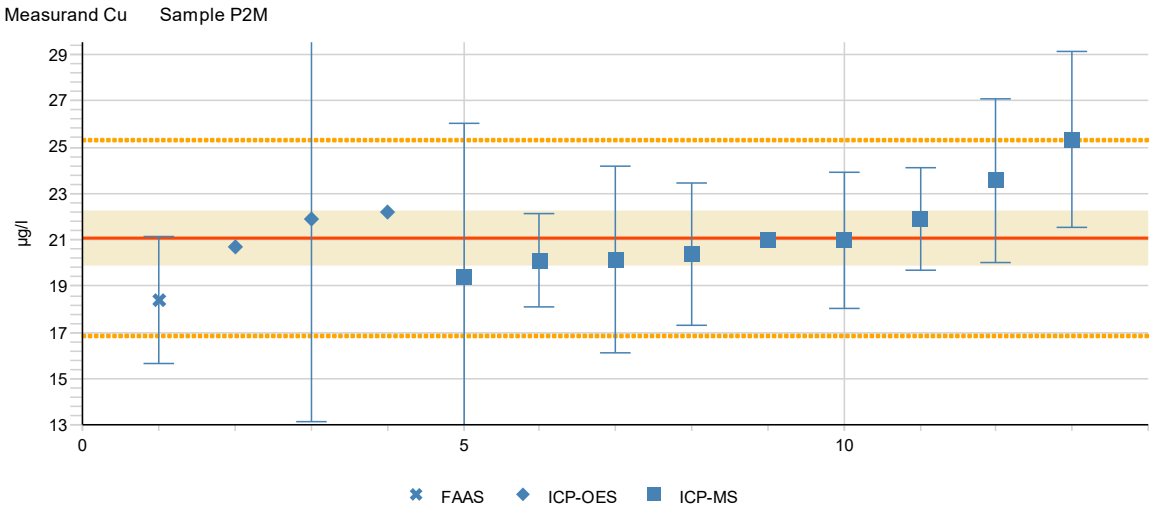


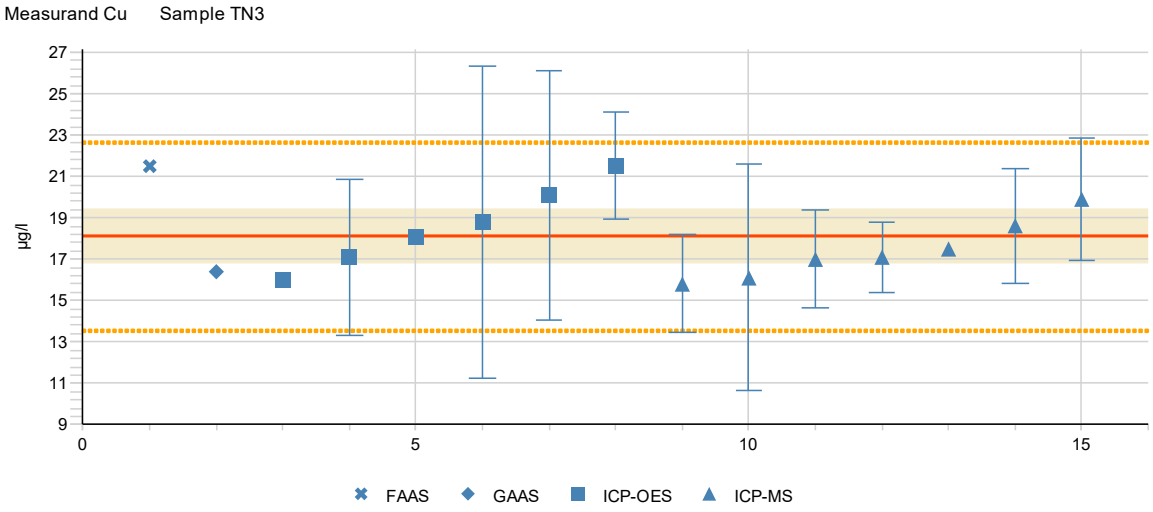
Measurand Cr Sample V4M

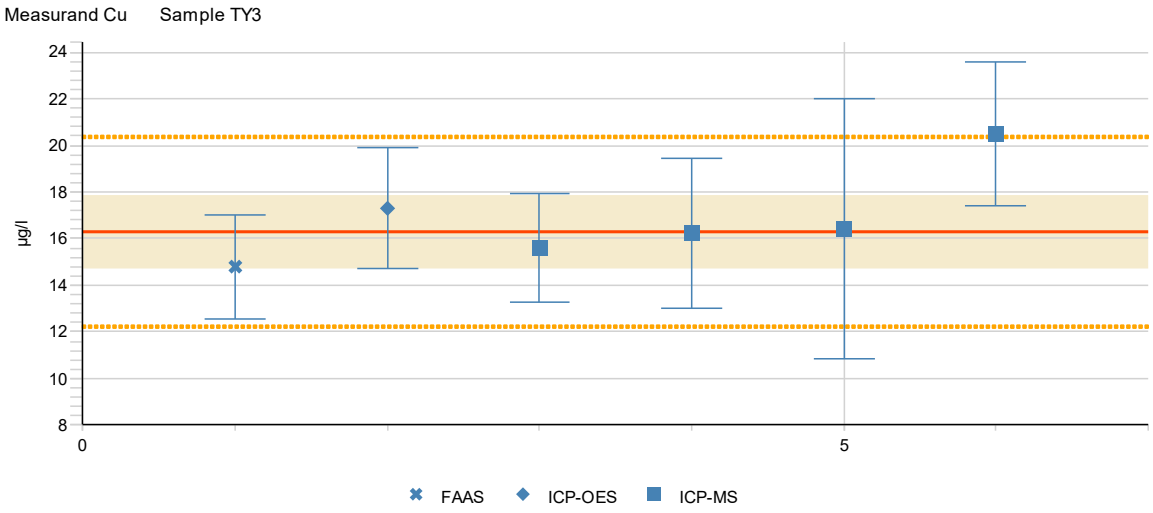


Measurand Cu Sample A1M

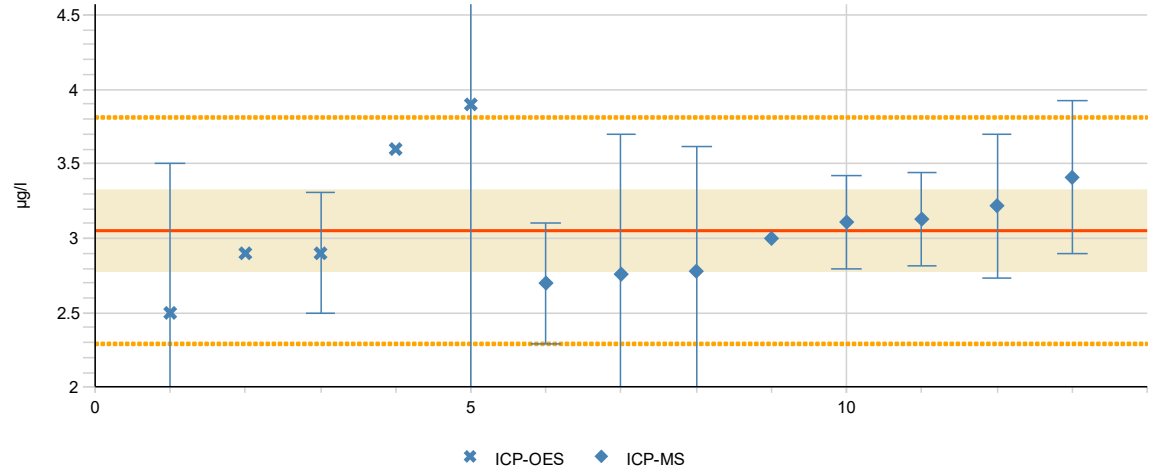



Measurand Cu Sample P2M
µg/l
29
27
25
23
21
19
17
15
13
0
5
10
FAAS
ICP-OES
ICP-MS

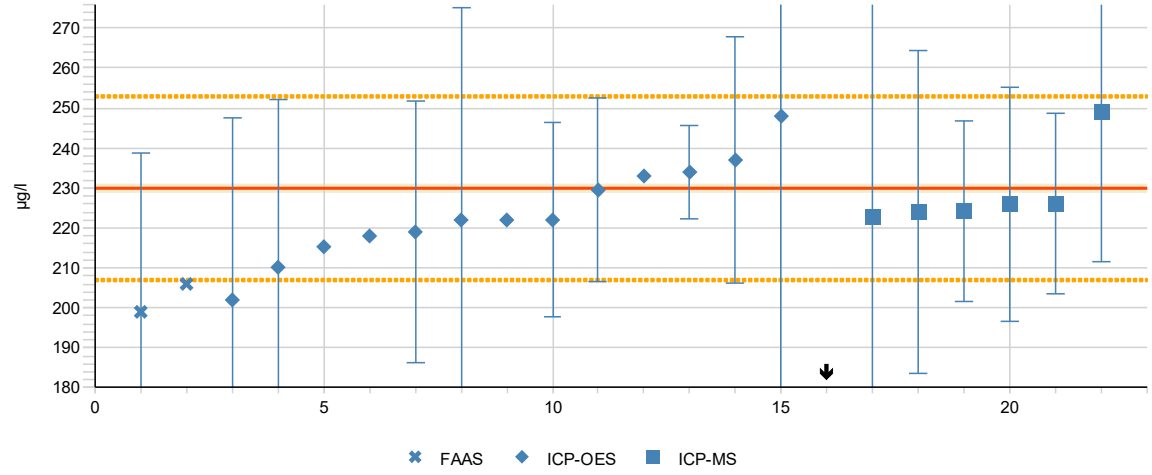

Measurand Cu Sample TN3
µg/l
27
25
23
21
19
17
15
13
11
9
0
5
10
15
FAAS
GAAS
ICP-OES
ICP-MS


Measurand Cu Sample TY3
µg/l
24
22
20
18
16
14
12
10
8
0
5
FAAS
ICP-OES
ICP-MS

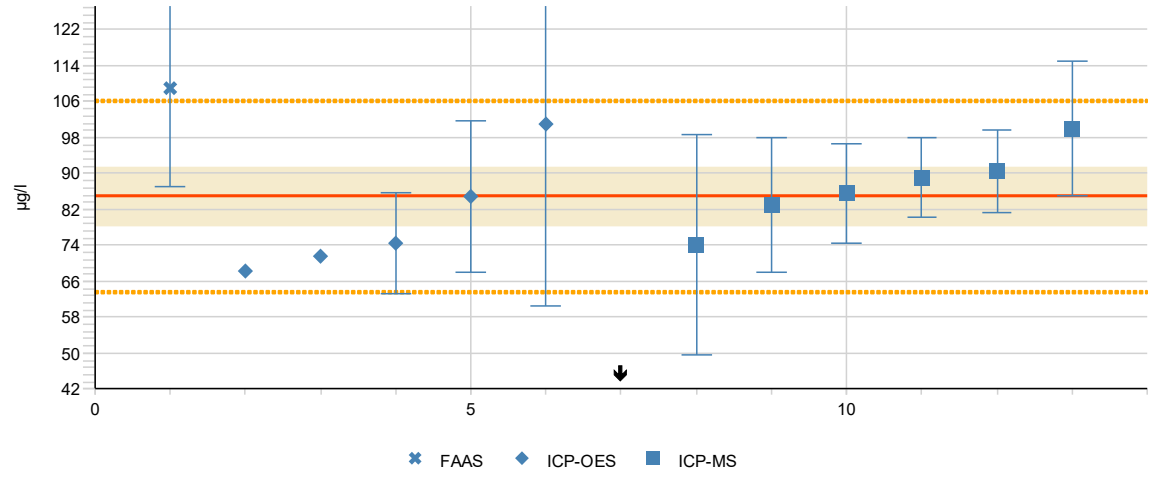
Measurand Cu Sample V4M

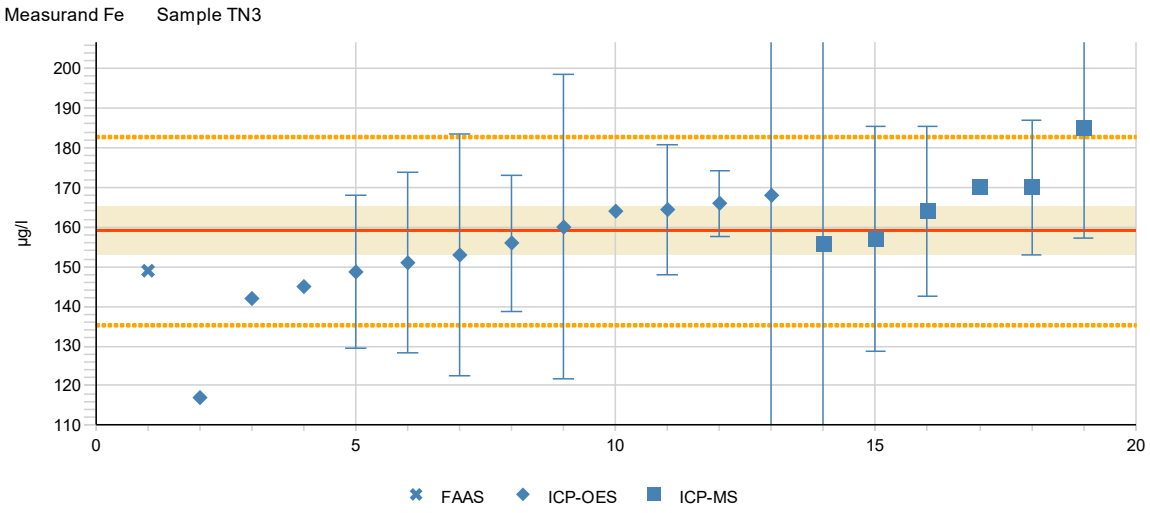


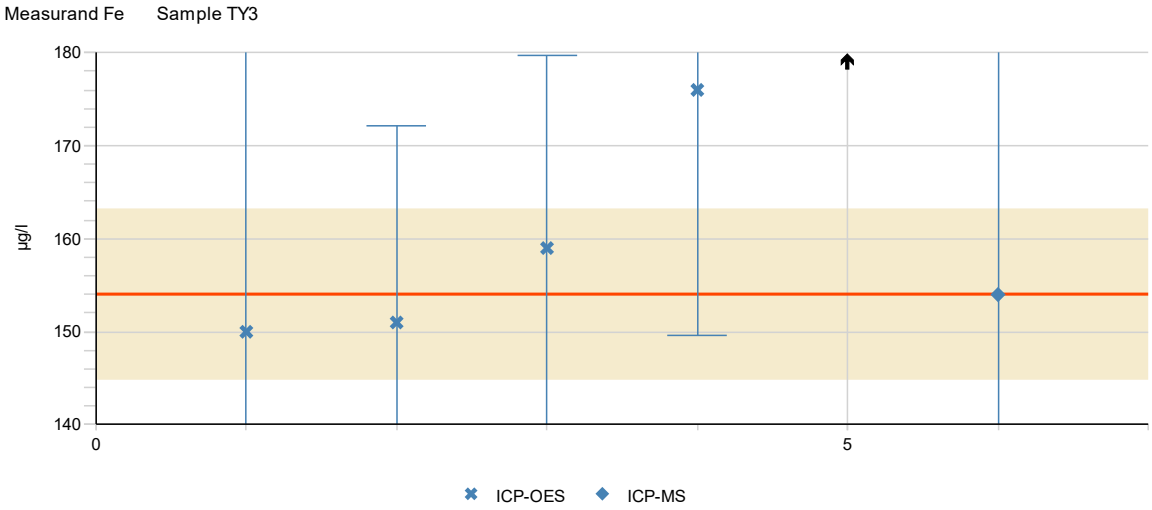
Measurand Fe Sample A1M

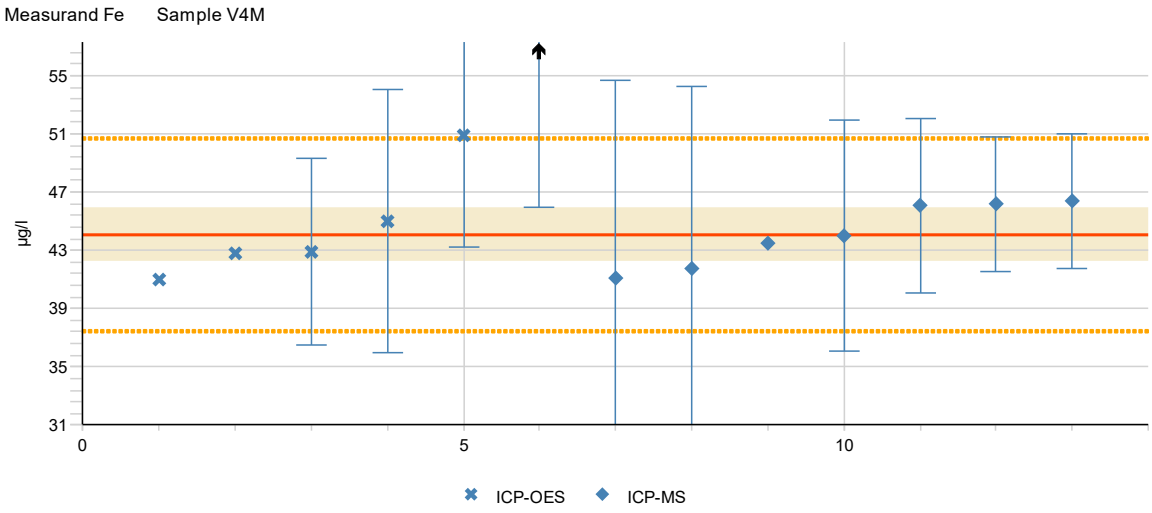


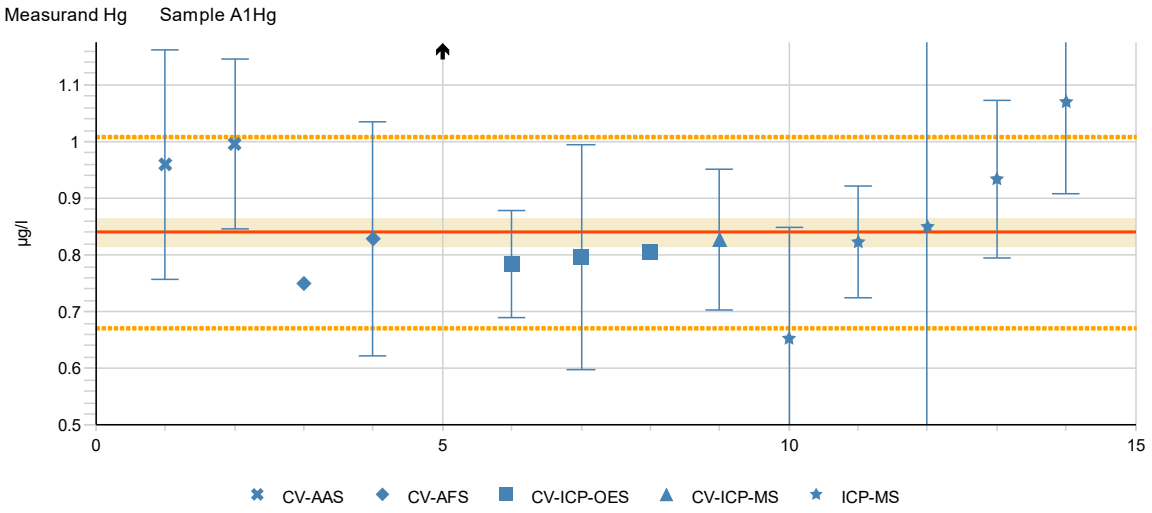
Measurand Fe Sample P2M

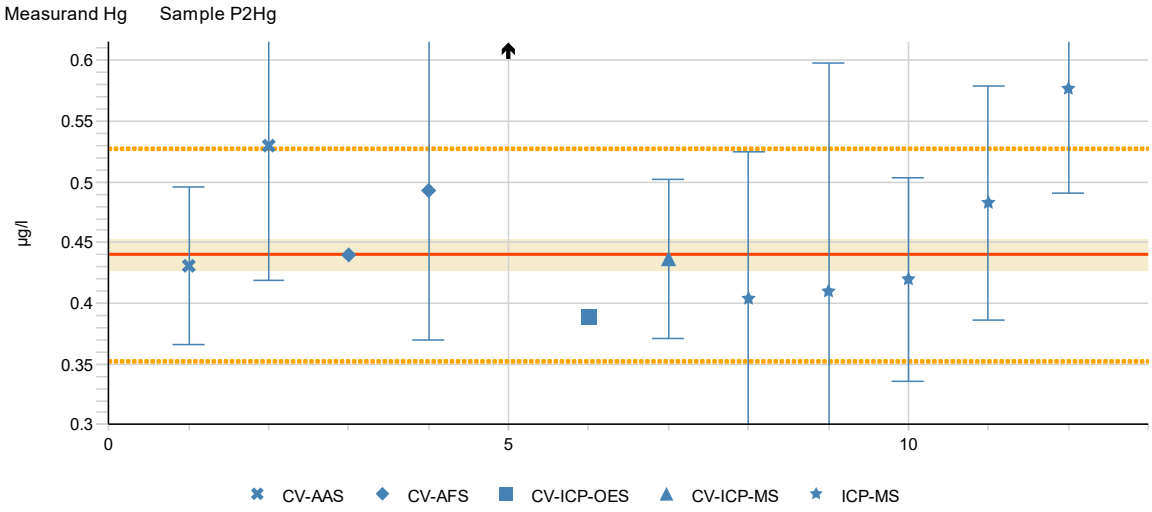


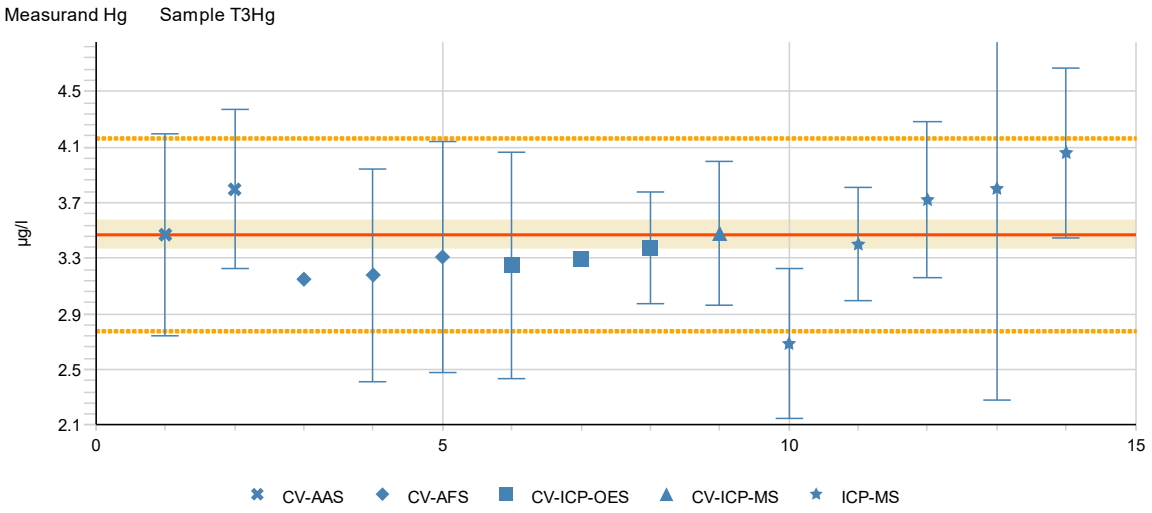

Measurand Fe Sample TN3
µg/l
200
190
180
170
160
150
140
130
120
110
0
5
10
15
20
FAAS
ICP-OES
ICP-MS


Measurand Fe Sample TY3
µg/l
180
170
160
150
140
0
5
ICP-OES
ICP-MS

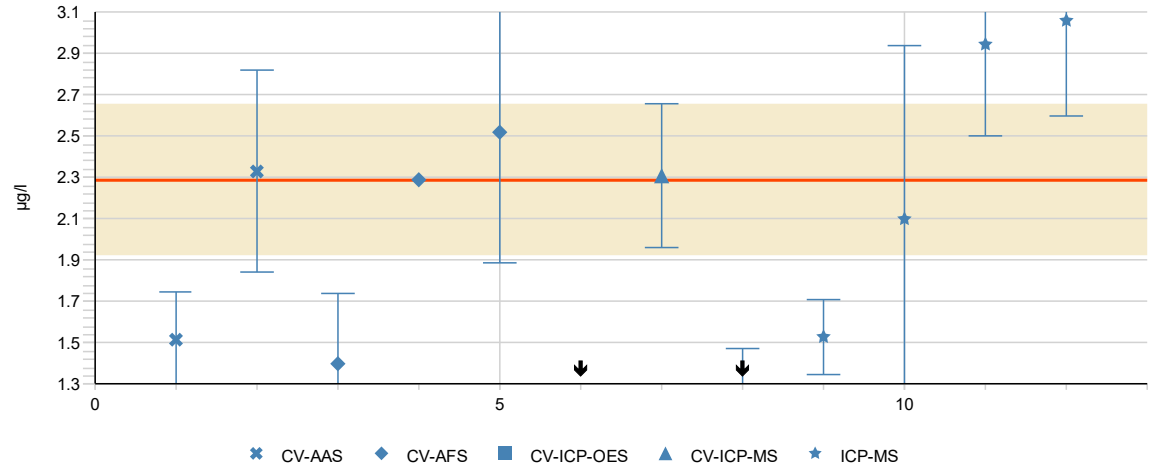

Measurand Fe Sample V4M
µg/l
55
51
47
43
39
35
31
0
5
10
ICP-OES
ICP-MS


Measurand Hg Sample A1Hg
µg/l
1.1
1
0.9
0.8
0.7
0.6
0.5
0
5
10
15
CV-AAS
CV-AFS
CV-ICP-OES
CV-ICP-MS
ICP-MS

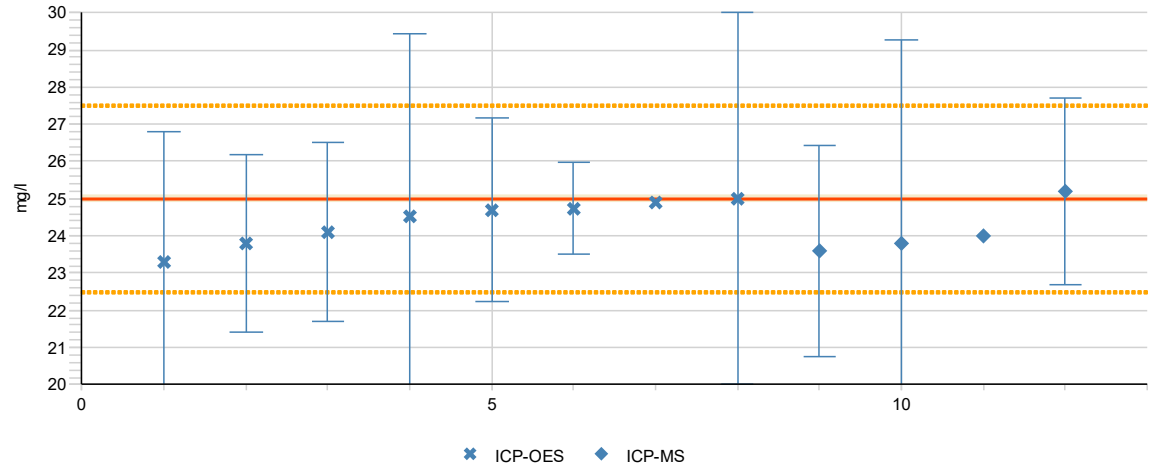

Measurand Hg Sample P2Hg
µg/l
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0
5
10
CV-AAS
CV-AFS
CV-ICP-OES
CV-ICP-MS
ICP-MS


Measurand Hg Sample T3Hg
µg/l
4.5
4.1
3.7
3.3
2.9
2.5
2.1
0
5
10
15
CV-AAS
CV-AFS
CV-ICP-OES
CV-ICP-MS
ICP-MS

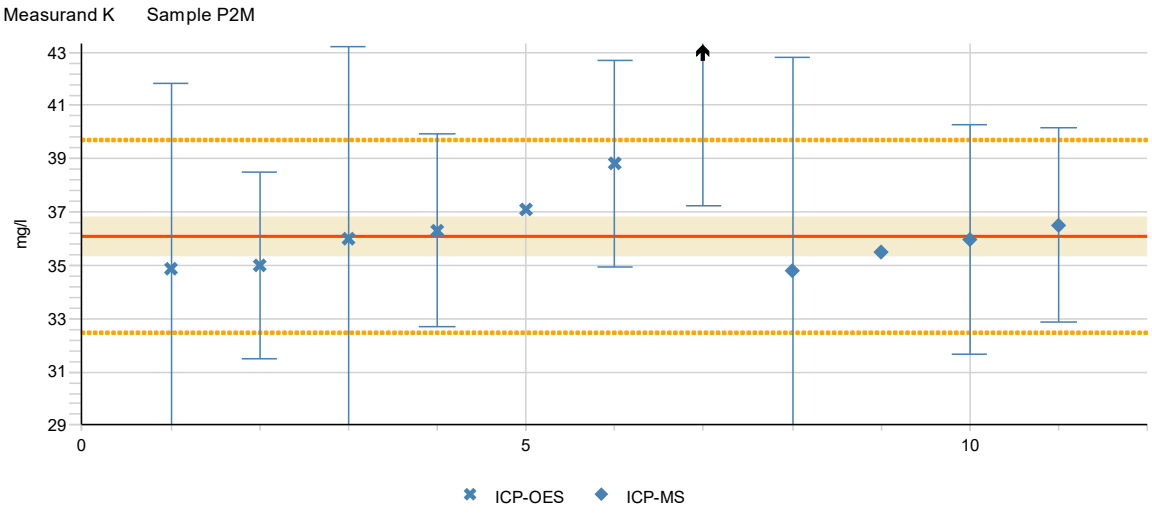
Measurand Hg Sample V4Hg



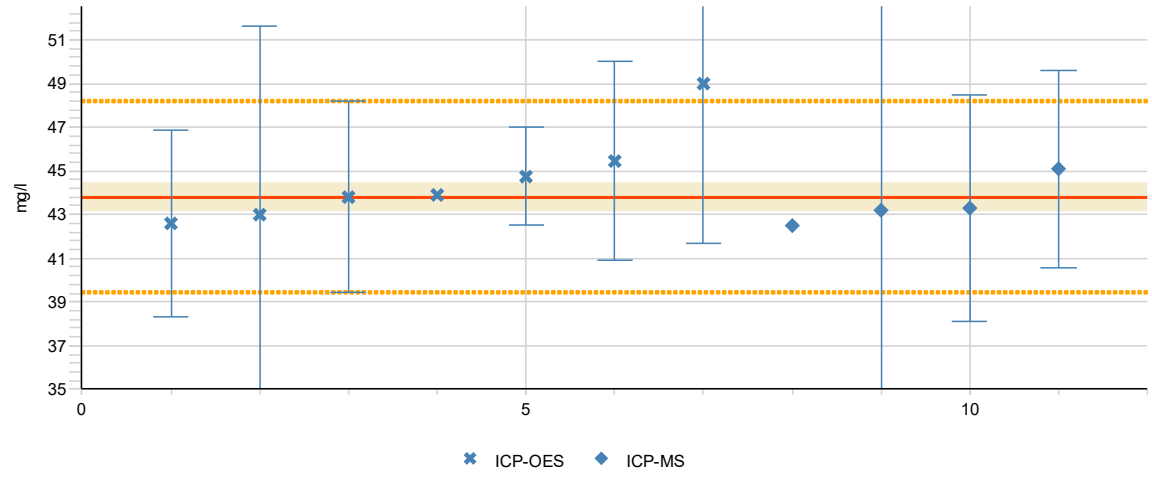
Measurand K Sample A1M



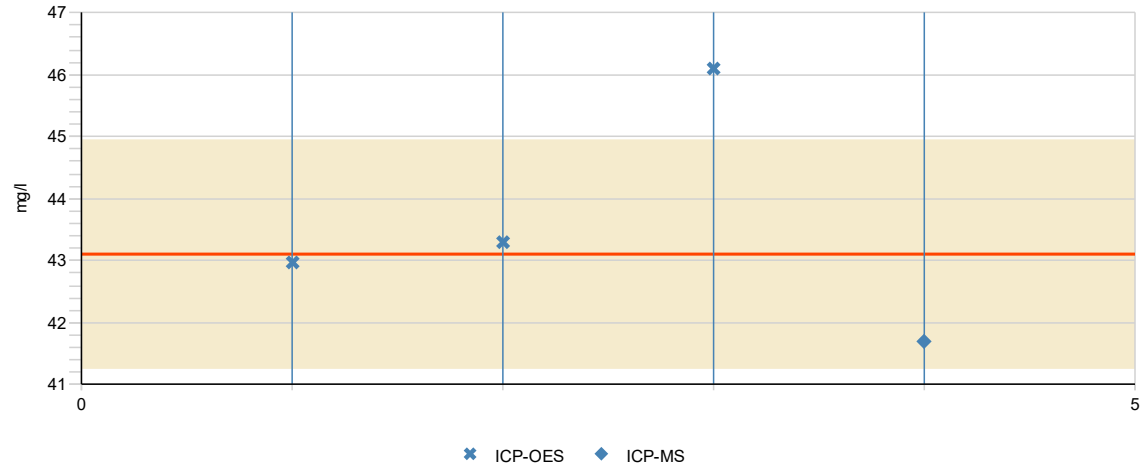
Measurand K Sample P2M



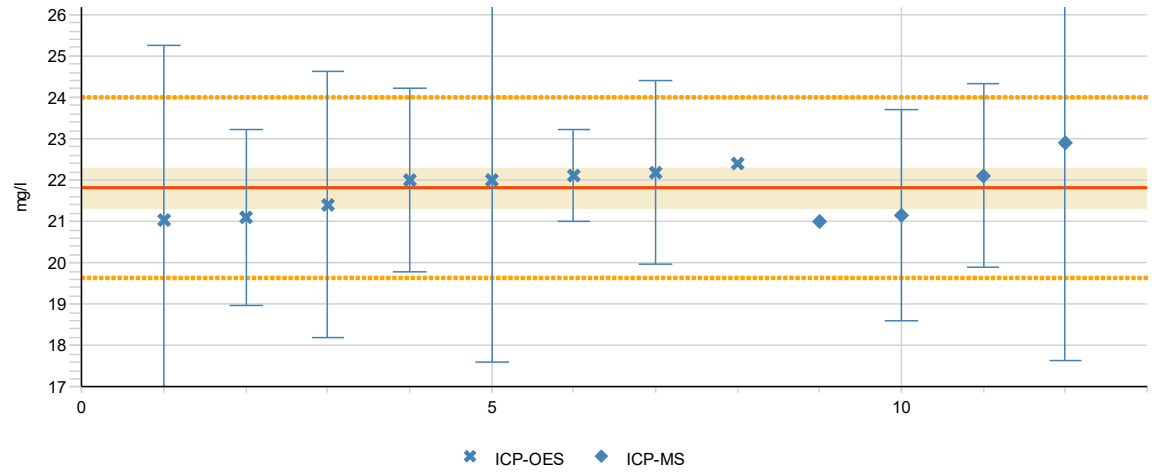
Measurand K Sample TN3

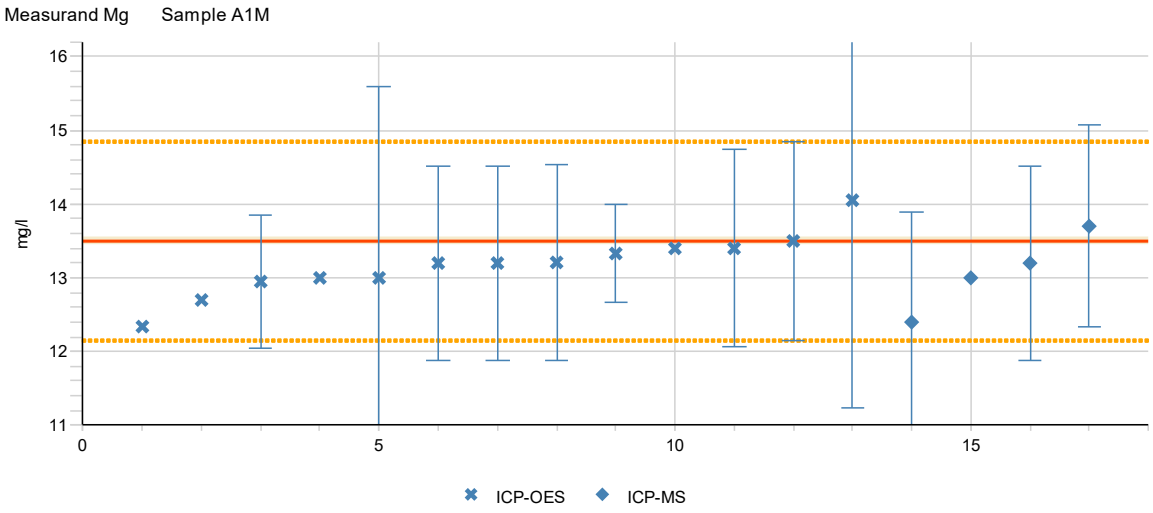


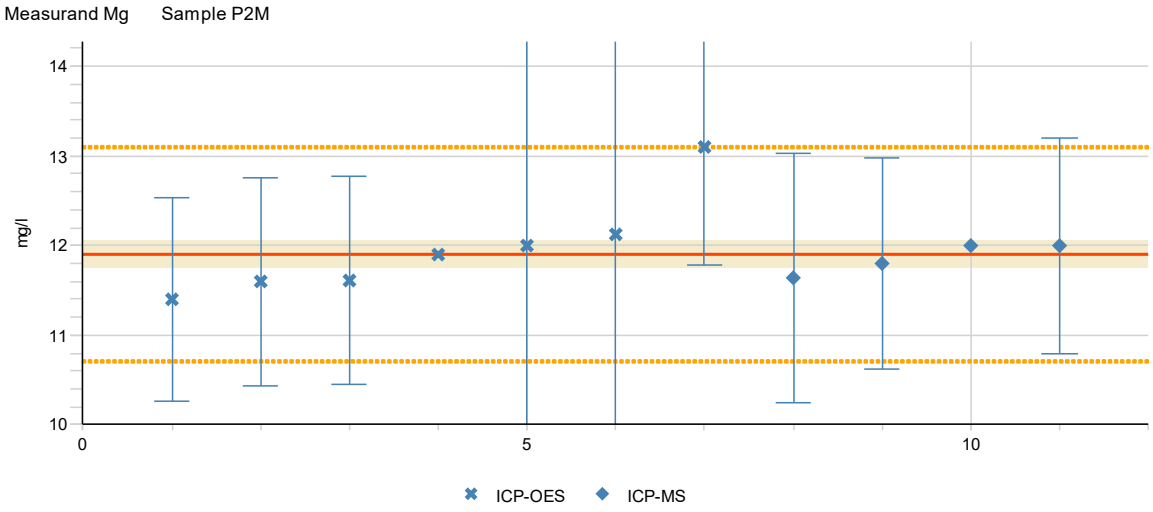
Measurand K Sample TY3

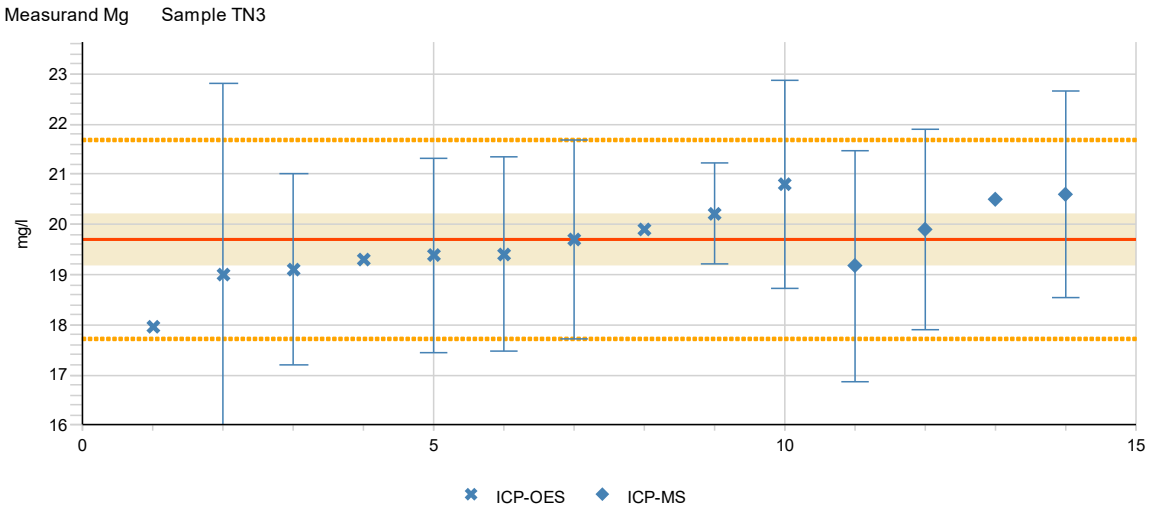


Measurand K Sample V4M

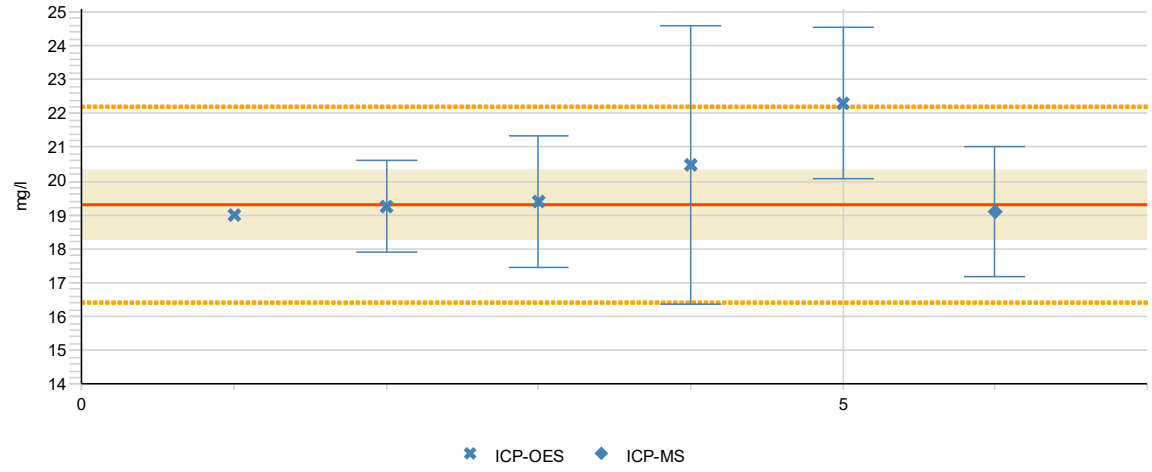



Measurand Mg Sample A1M
mg/l
16
15
14
13
12
11
0
5
10
15
ICP-OES
ICP-MS

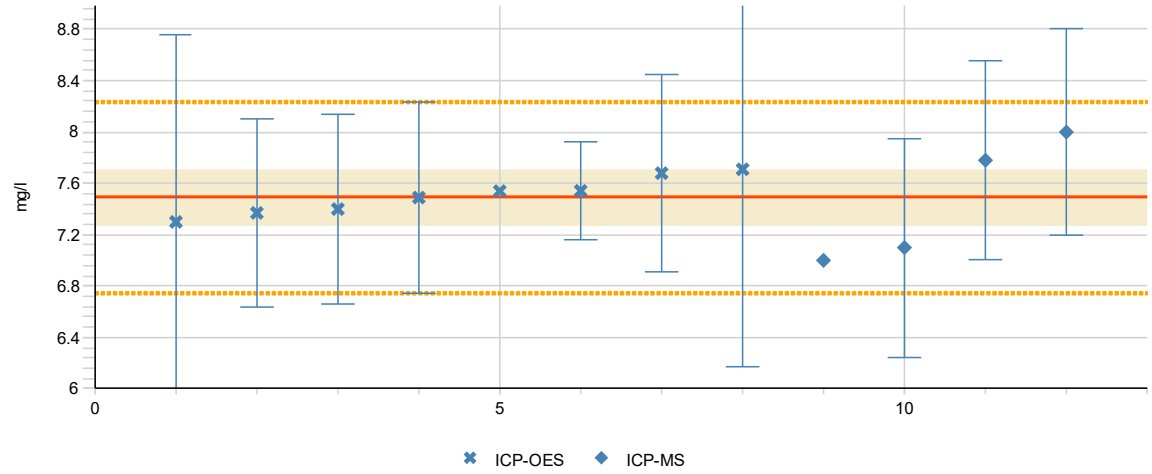

Measurand Mg Sample P2M
mg/l
14
13
12
11
10
0
5
10
ICP-OES
ICP-MS


Measurand Mg Sample TN3
mg/l
23
22
21
20
19
18
17
16
0
5
10
15
ICP-OES
ICP-MS

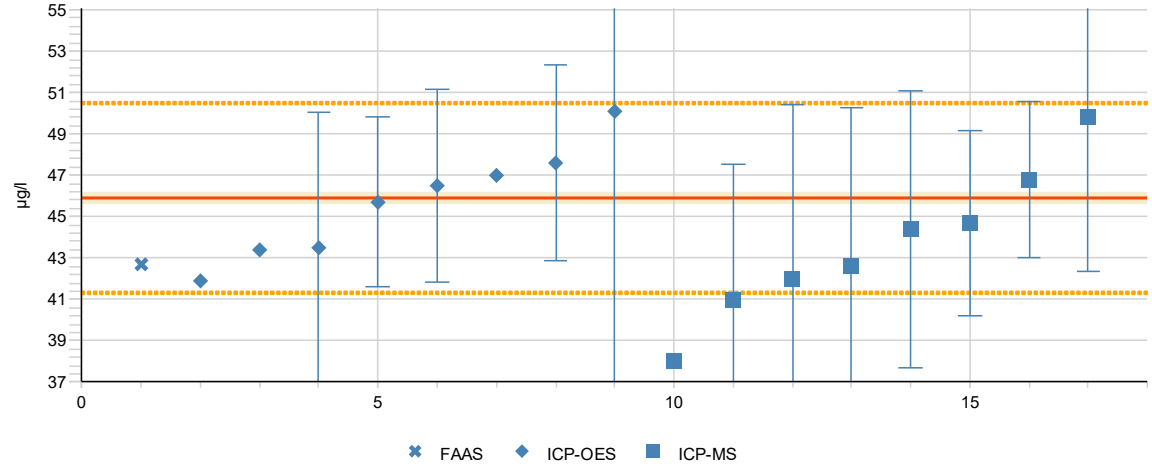
Measurand Mg Sample TY3

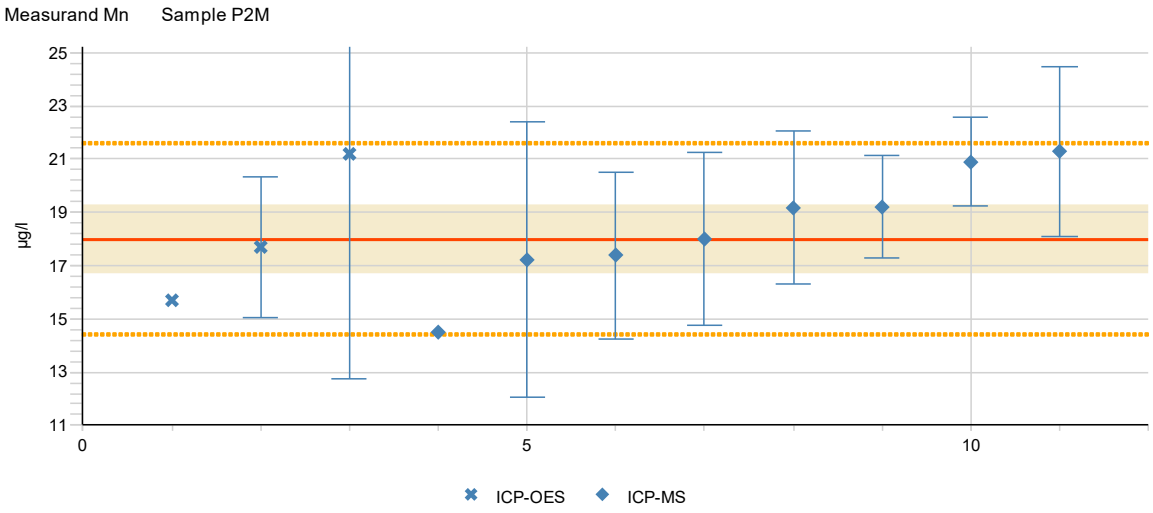


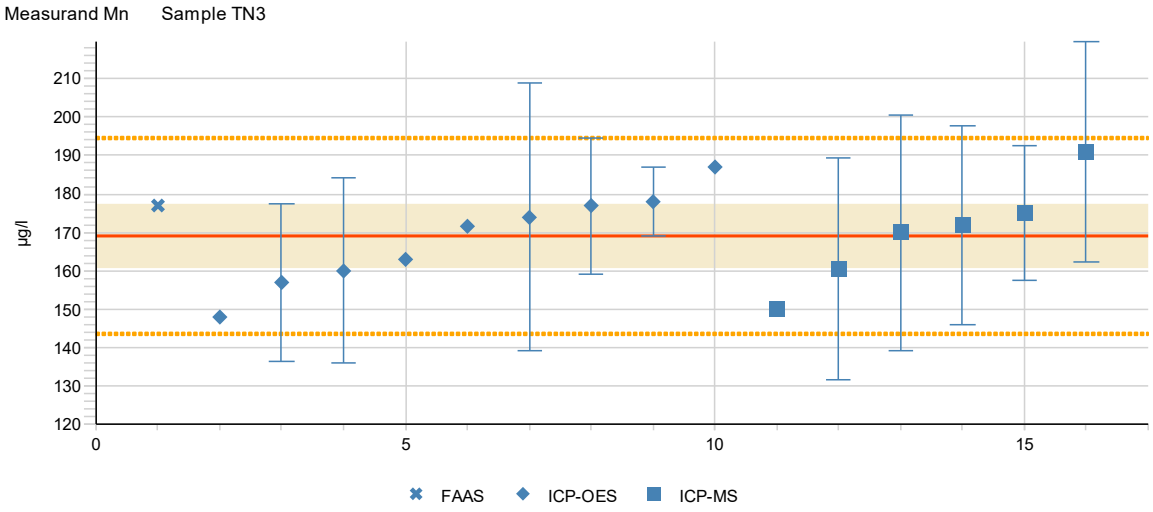
Measurand Mg Sample V4M

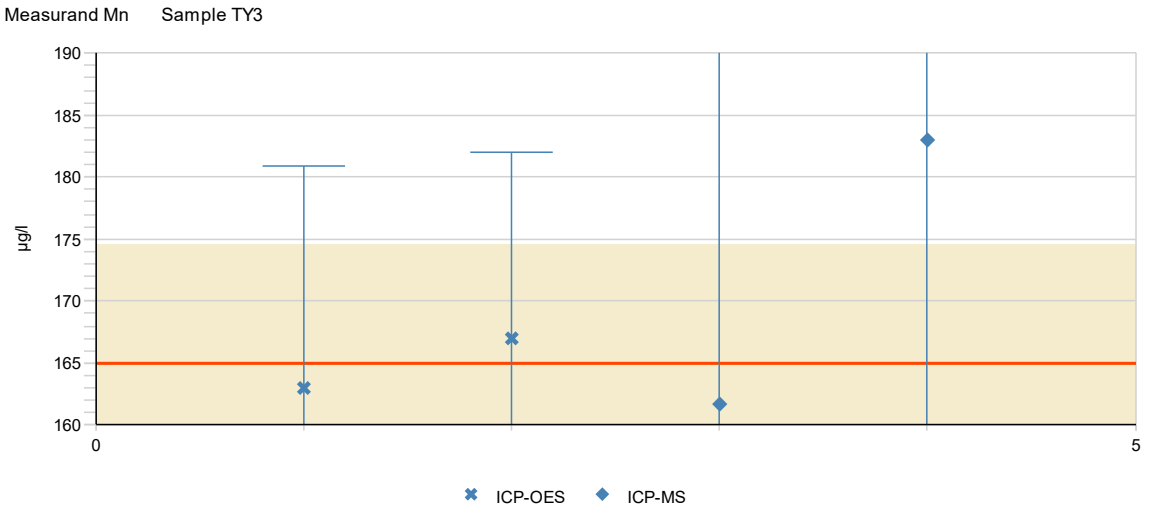


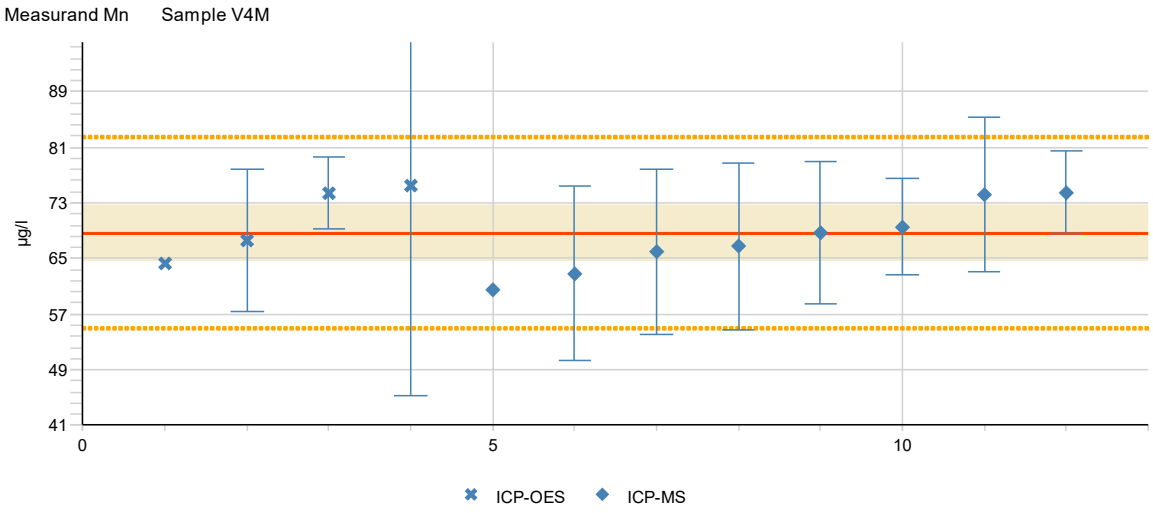
Measurand Mn Sample A1M

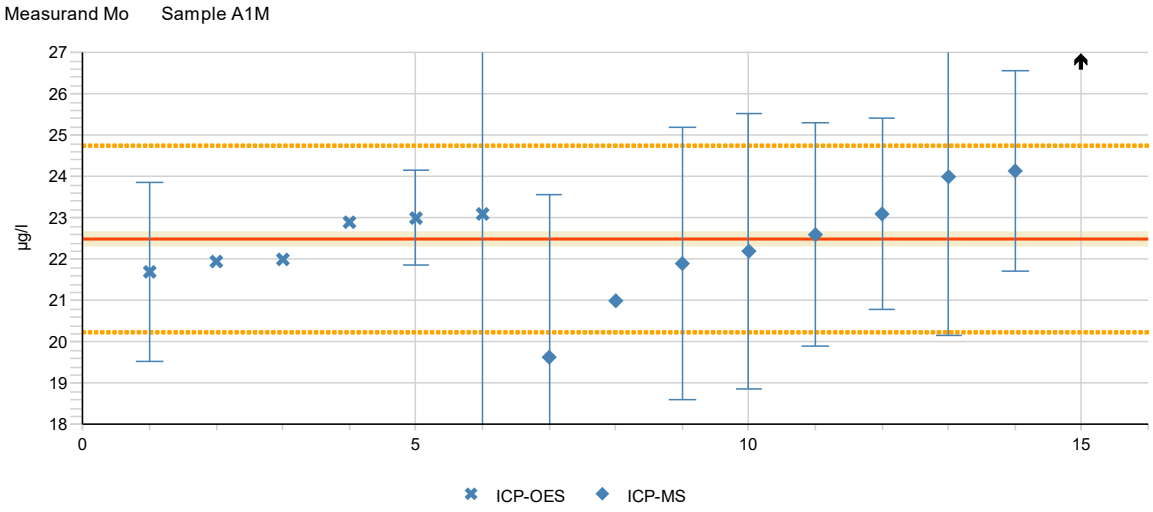


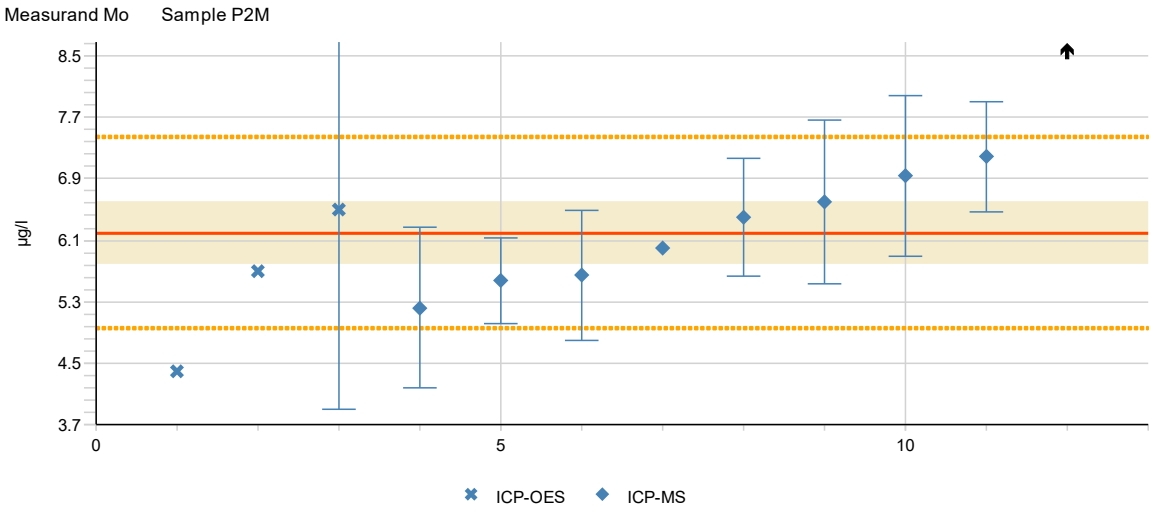

Measurand Mn Sample P2M
µg/l
25
23
21
19
17
15
13
11
0
5
10
ICP-OES
ICP-MS

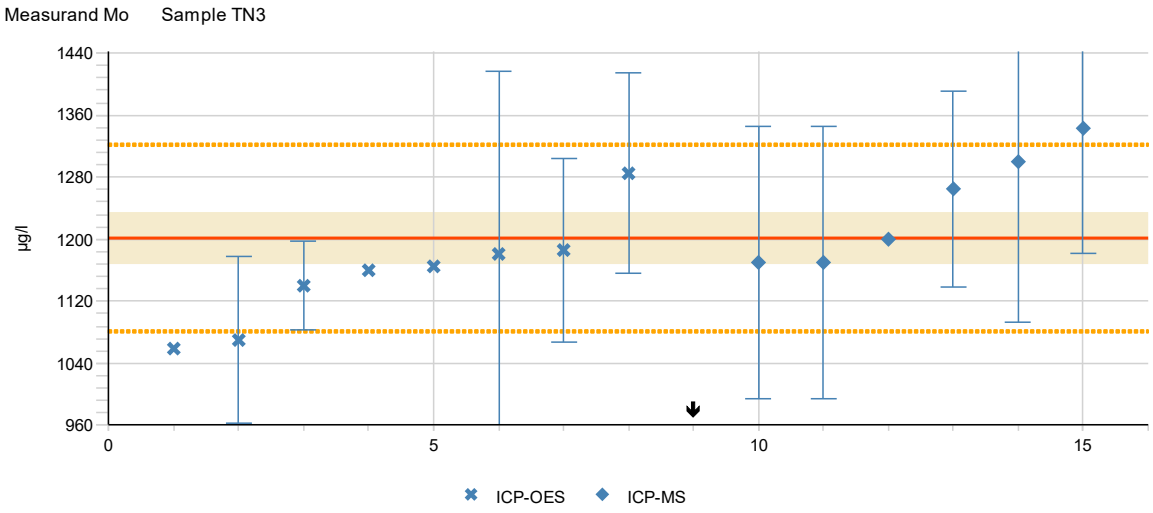

Measurand Mn Sample TN3
µg/l
210
200
190
180
170
160
150
140
130
120
0
5
10
15
FAAS
ICP-OES
ICP-MS

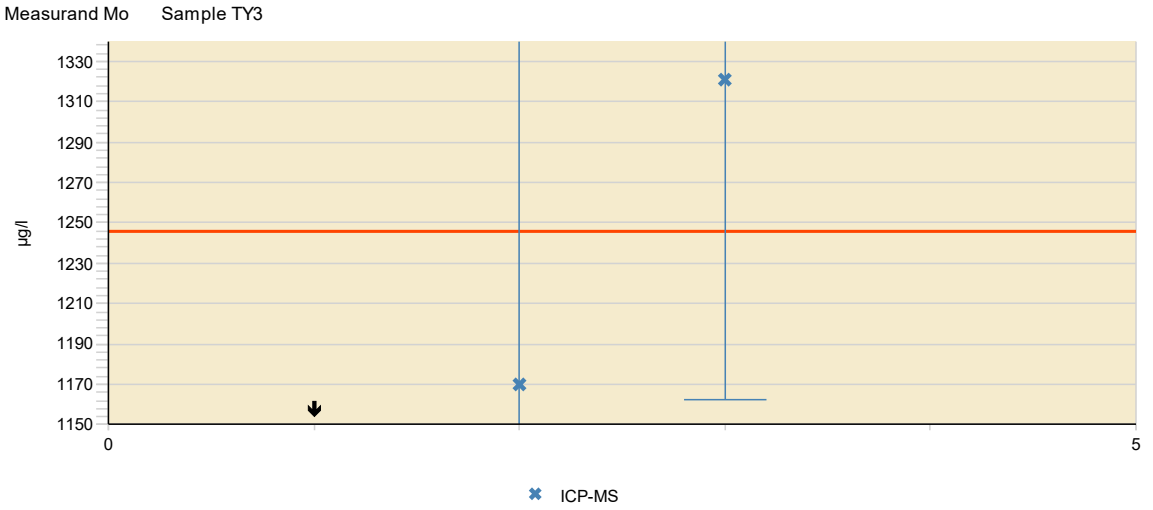

Measurand Mn Sample TY3
µg/l
190
185
180
175
170
165
160
0
5
ICP-OES
ICP-MS

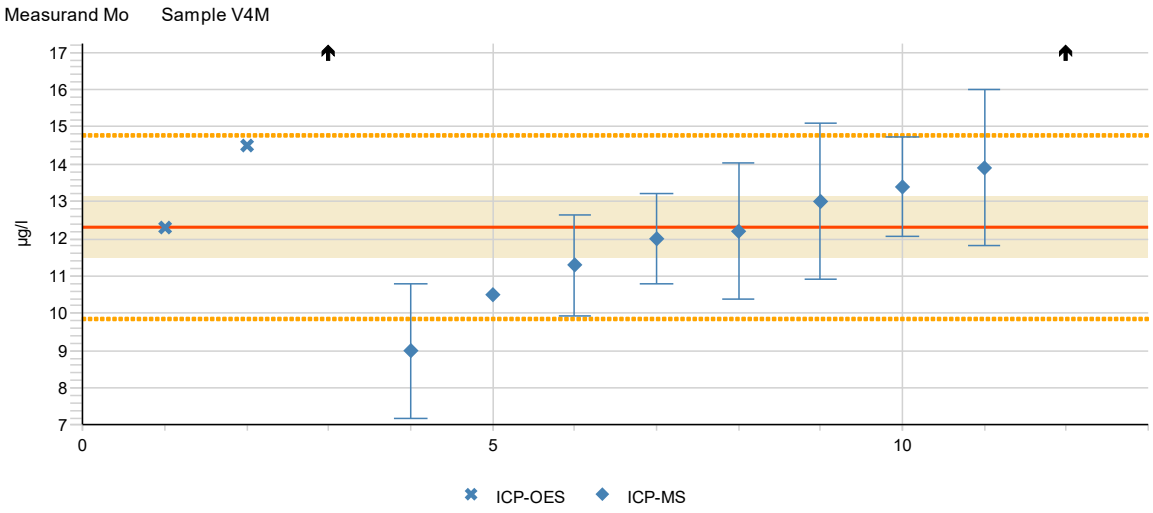

Measurand Mn Sample V4M
µg/l
89
81
73
65
57
49
41
0
5
10
ICP-OES
ICP-MS


Measurand Mo Sample A1M
µg/l
27
26
25
24
23
22
21
20
19
18
0
5
10
15
ICP-OES
ICP-MS

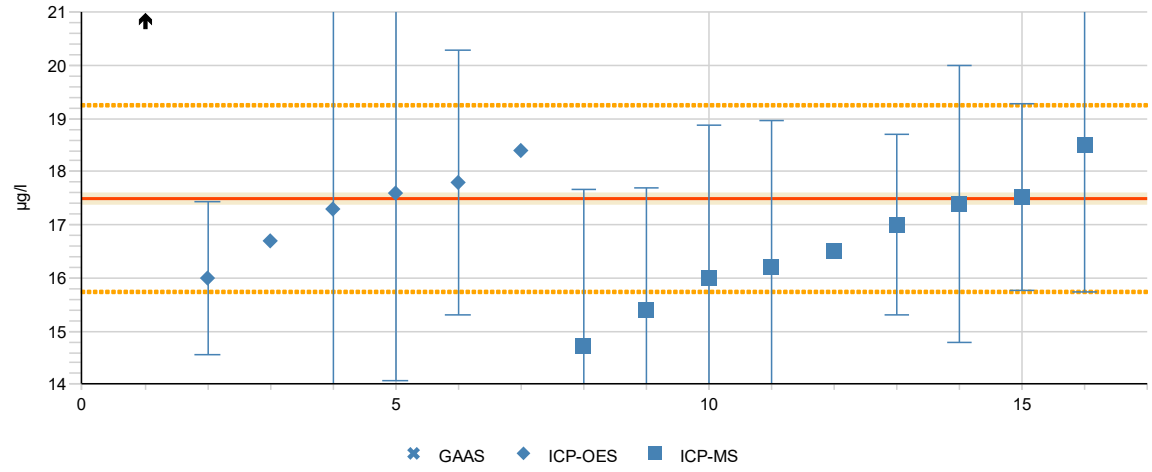

Measurand Mo Sample P2M
µg/l
8.5
7.7
6.9
6.1
5.3
4.5
3.7
0
5
10
ICP-OES
ICP-MS


Measurand Mo
Sample TN3
µg/l
1440
1360
1280
1200
1120
1040
960
0
5
10
15
ICP-OES
ICP-MS

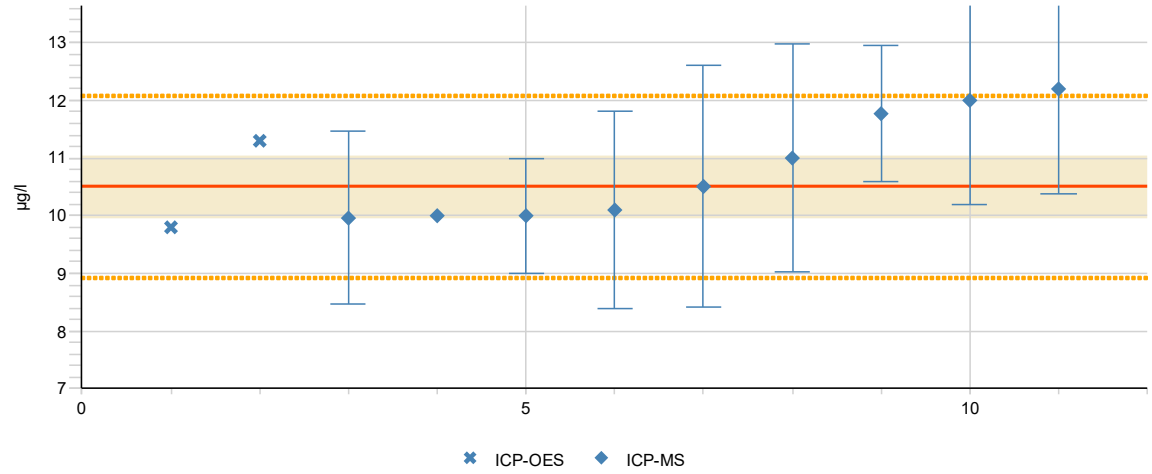

Measurand Mo
Sample TY3
µg/l
1330
1310
1290
1270
1250
1230
1210
1190
1170
1150
0
5
ICP-MS


Measurand Mo
Sample V4M
µg/l
17
16
15
14
13
12
11
10
9
8
7
0
5
10
ICP-OES
ICP-MS

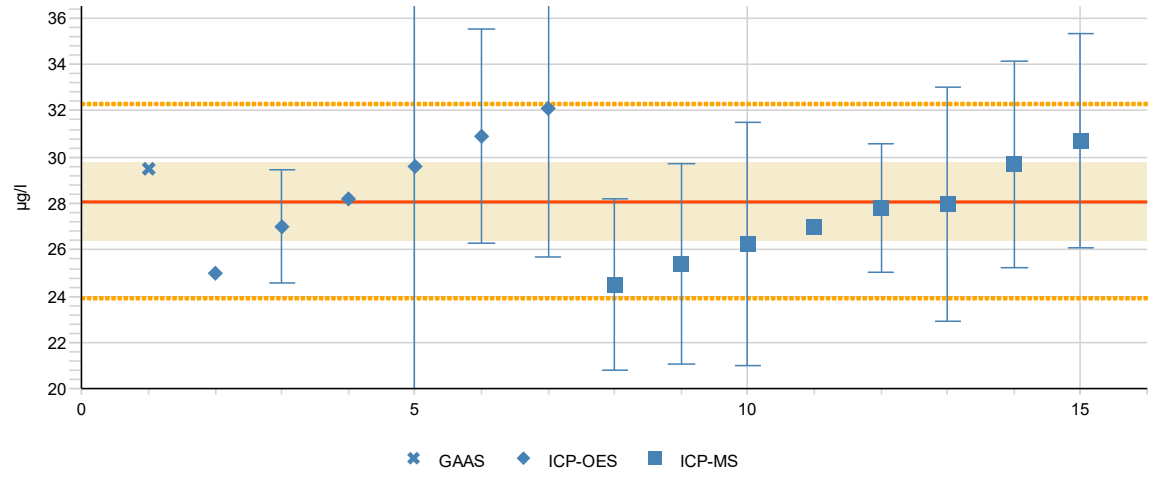
Measurand Ni Sample A1M



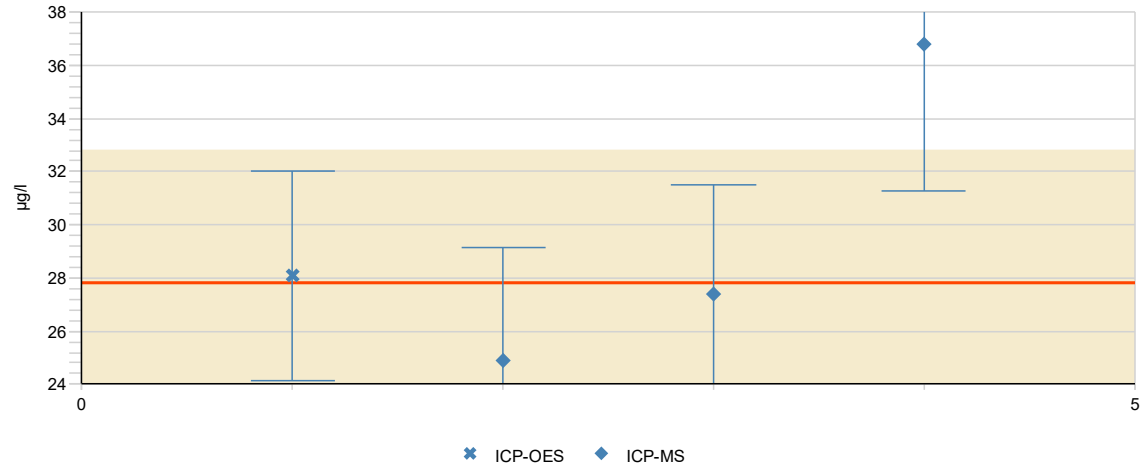
Measurand Ni Sample P2M



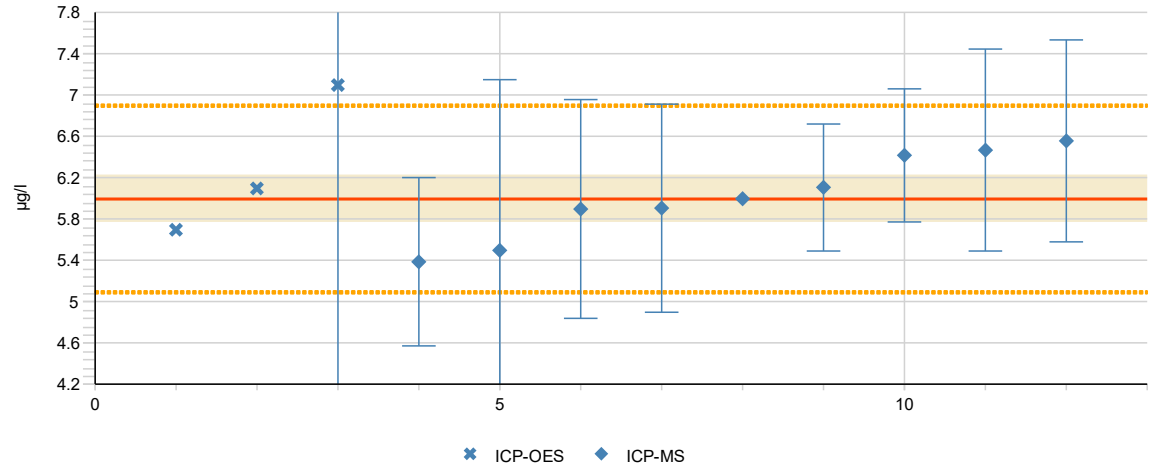
Measurand Ni Sample TN3



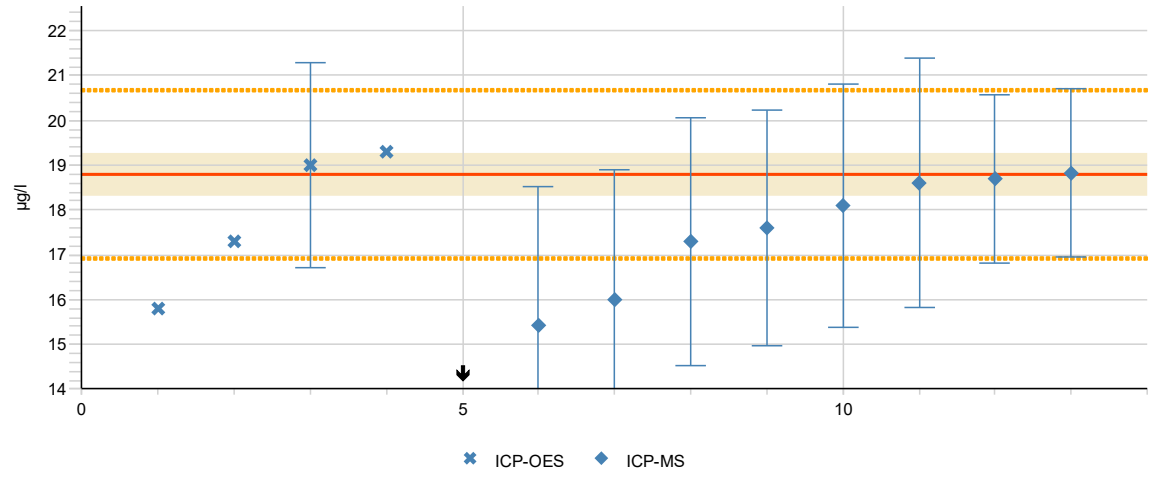
Measurand Ni Sample TY3

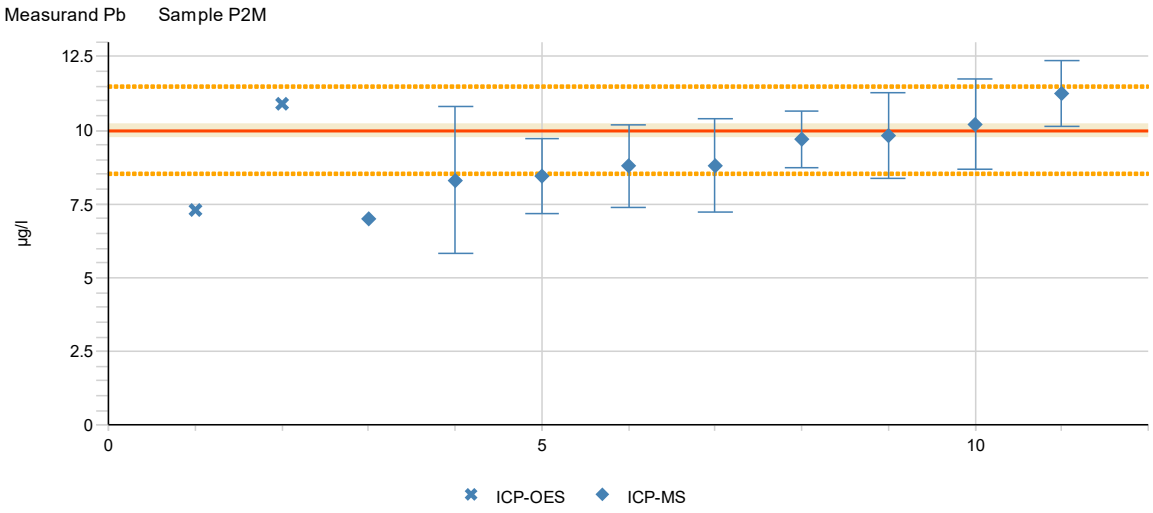


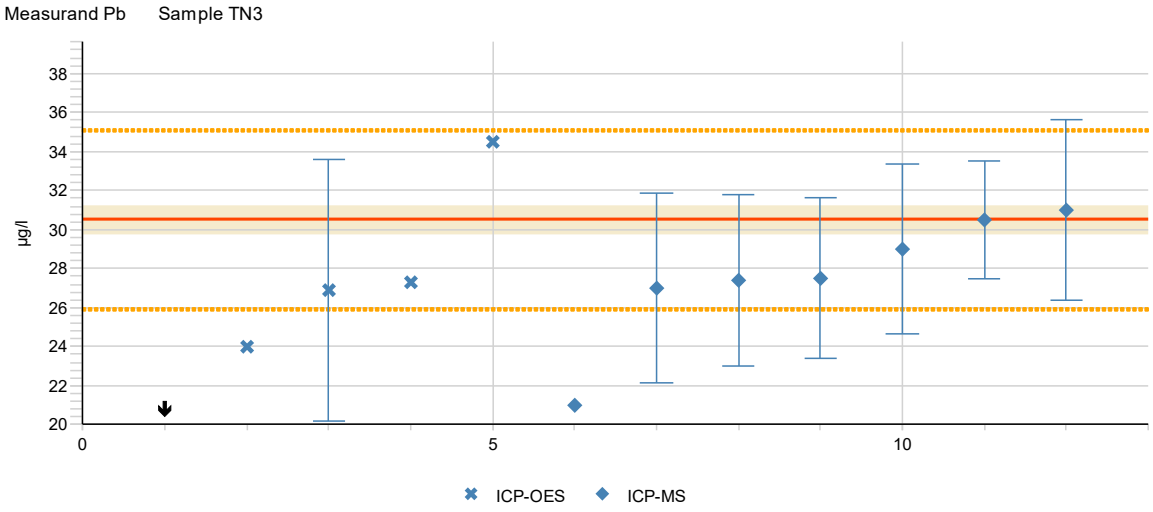
Measurand Ni Sample V4M

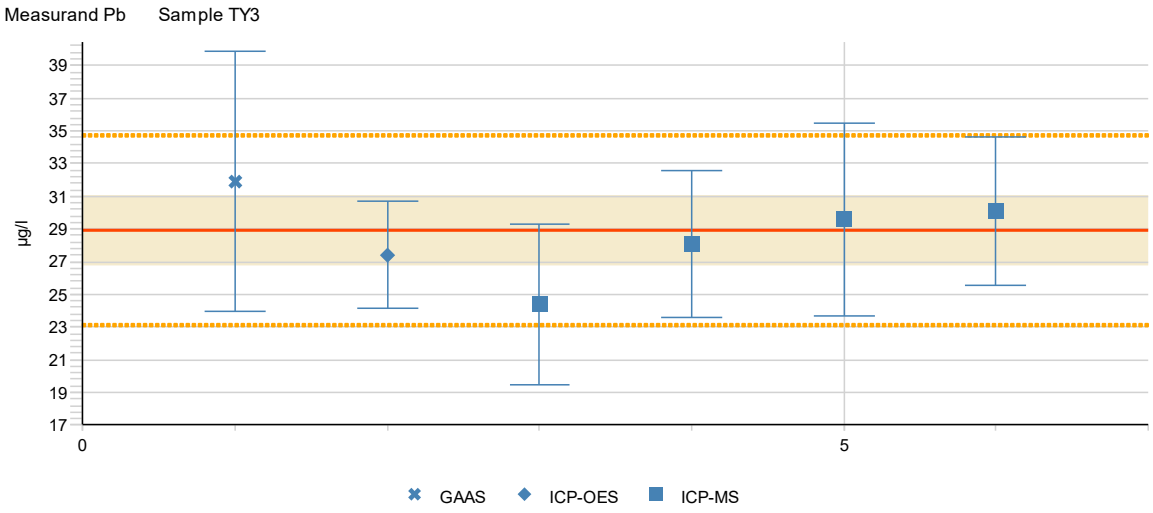


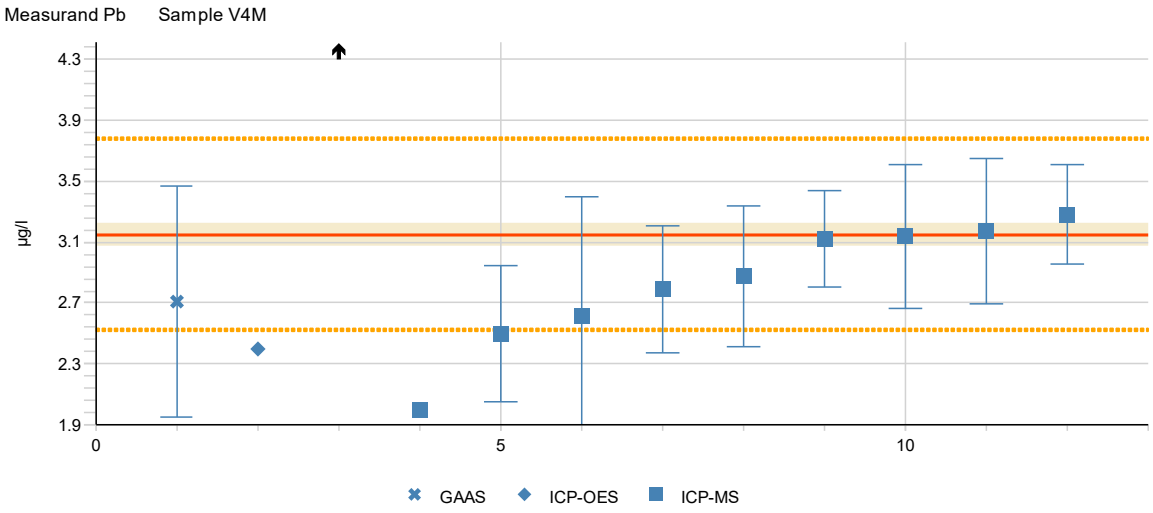
Measurand Pb Sample A1M

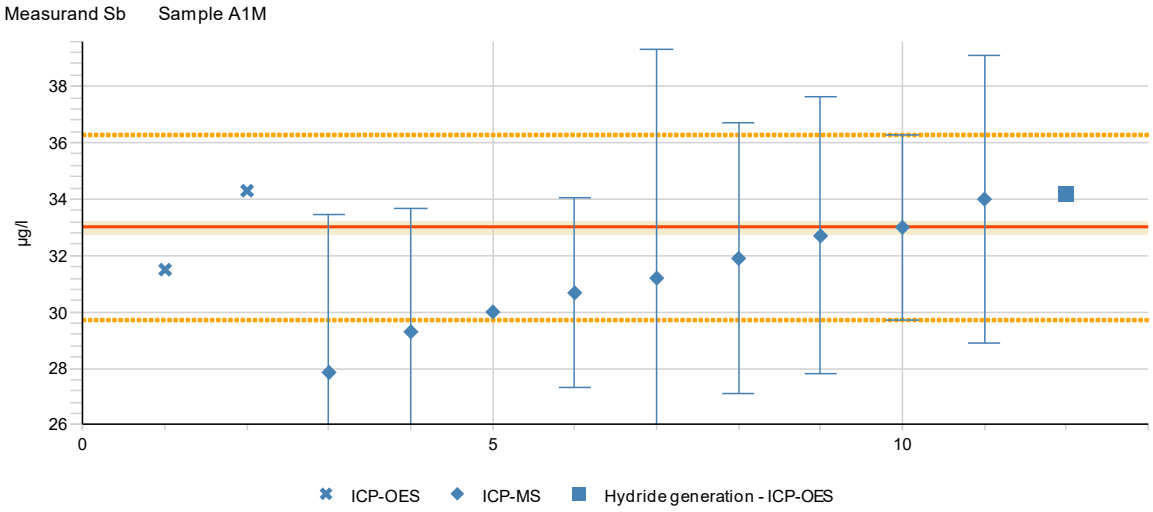


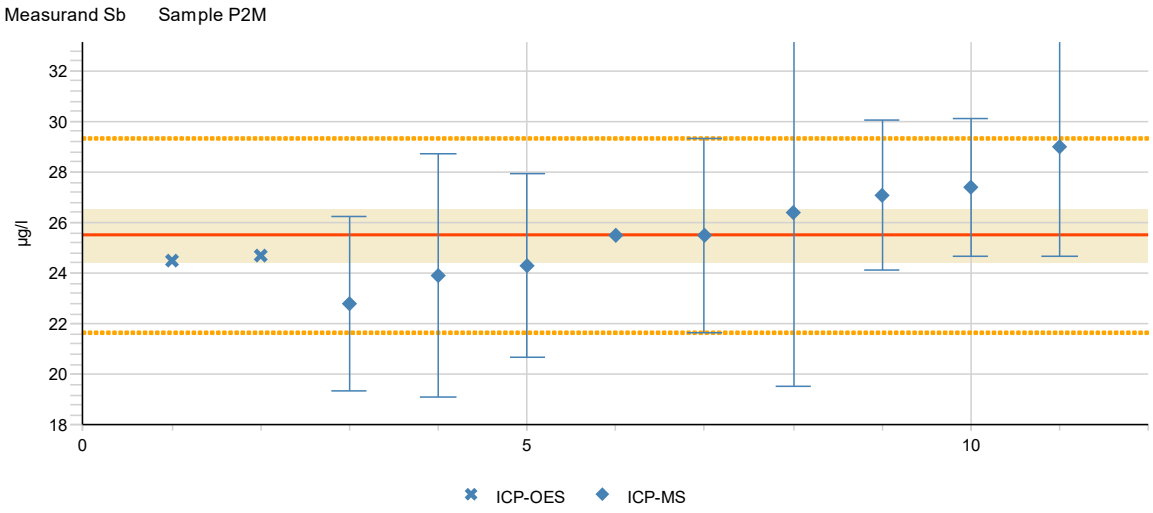

Measurand Pb Sample P2M
µg/l
12.5
10
7.5
5
2.5
0
0
5
10
ICP-OES
ICP-MS


Measurand Pb Sample TN3
µg/l
38
36
34
32
30
28
26
24
22
20
0
5
10
ICP-OES
ICP-MS

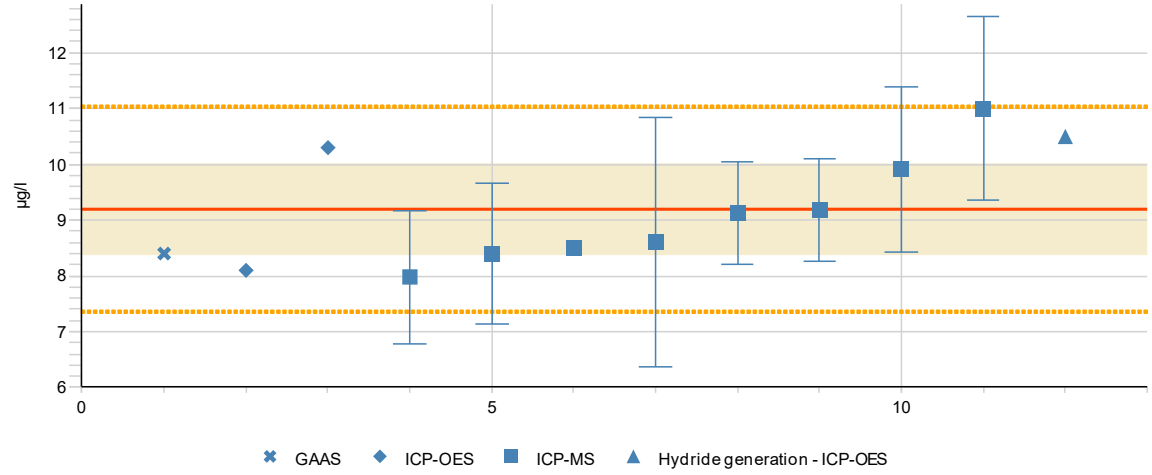

Measurand Pb Sample TY3
µg/l
39
37
35
33
31
29
27
25
23
21
19
17
0
5
GAAS
ICP-OES
ICP-MS


Measurand Pb Sample V4M
µg/l
4.3
3.9
3.5
3.1
2.7
2.3
1.9
0
5
10
GAAS
ICP-OES
ICP-MS

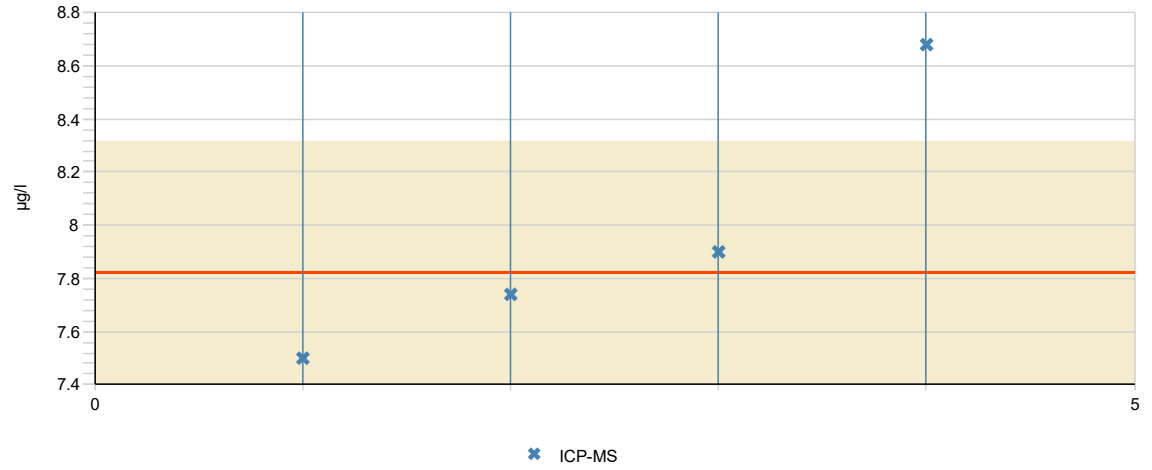

Measurand Sb Sample A1M
µg/l
38
36
34
32
30
28
26
0
5
10
ICP-OES
ICP-MS
Hydride generation - ICP-OES


Measurand Sb Sample P2M
µg/l
32
30
28
26
24
22
20
18
0
5
10
ICP-OES
ICP-MS

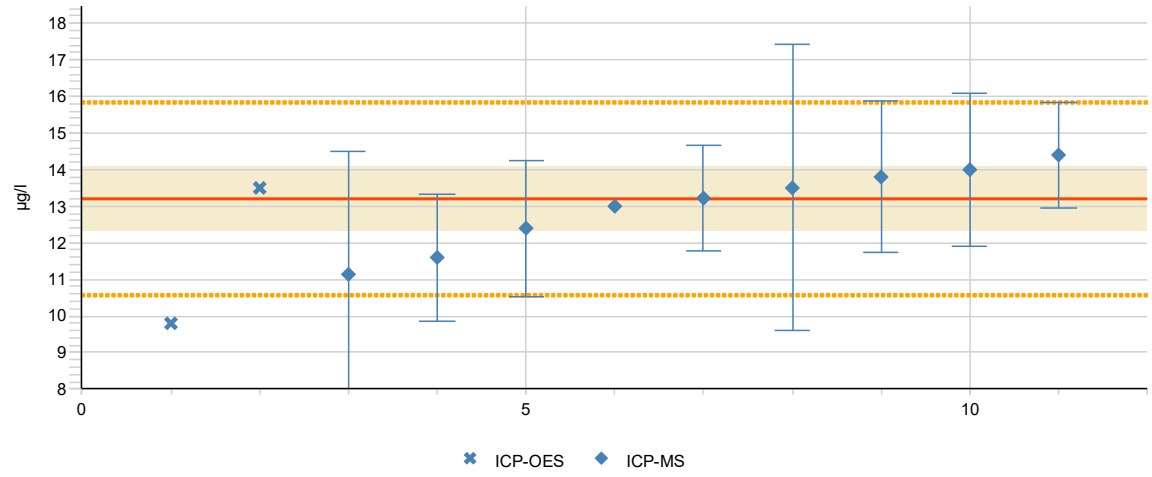
Measurand Sb Sample TN3

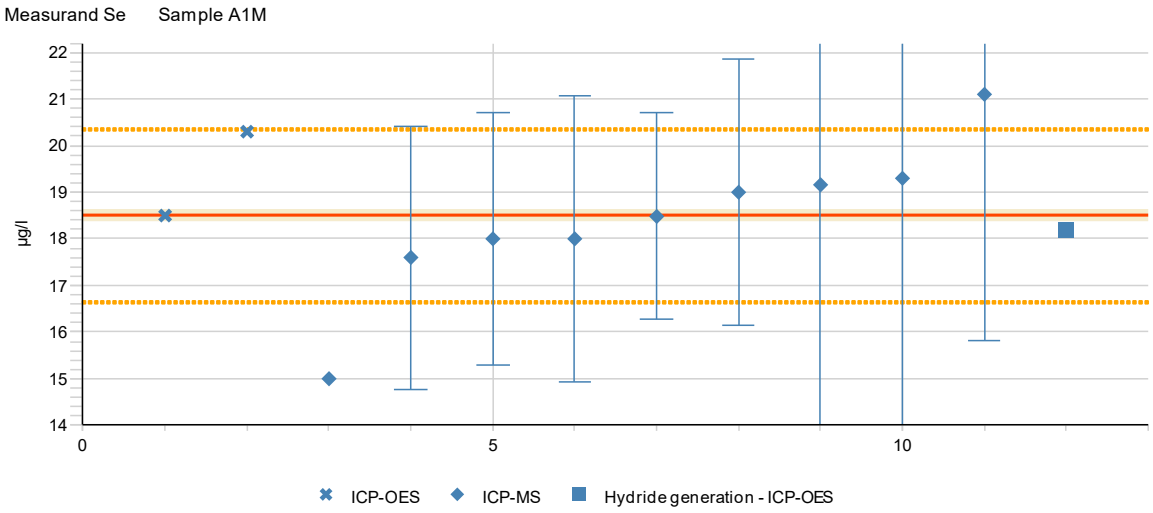


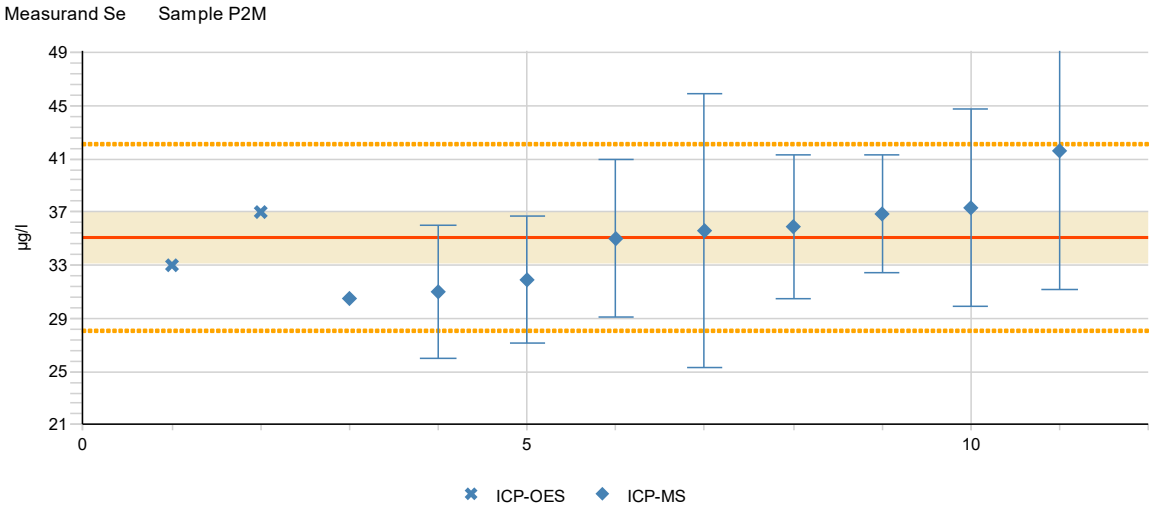
Measurand Sb Sample TY3

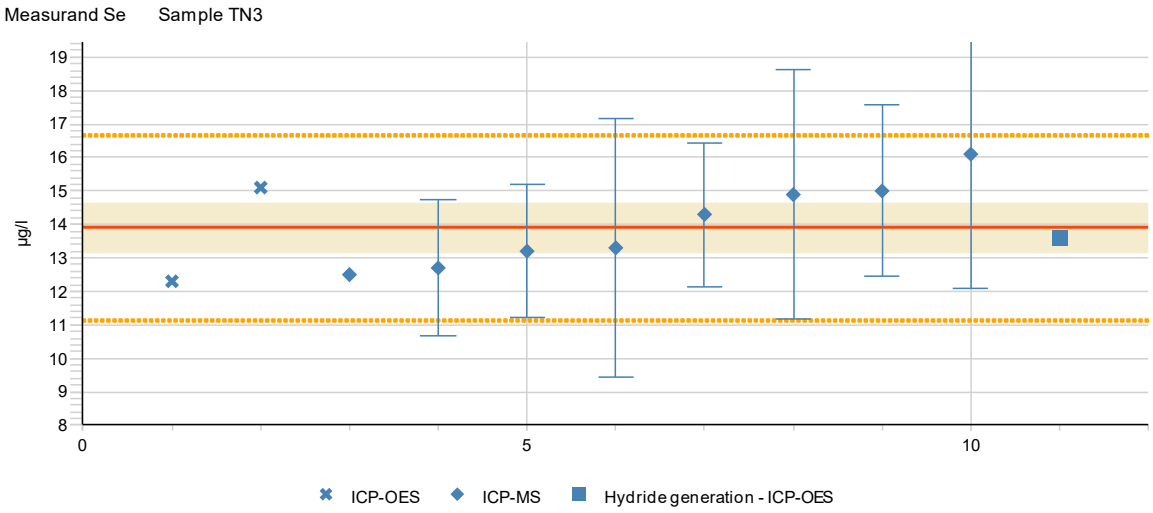


Measurand Sb Sample V4M

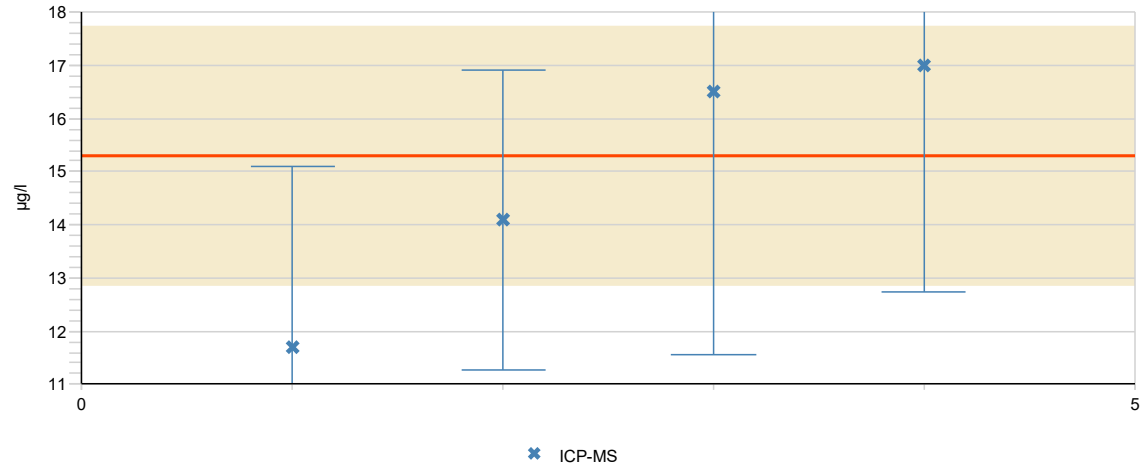



Measurand Se Sample A1M
µg/l
22
21
20
19
18
17
16
15
14
0
5
10
ICP-OES
ICP-MS
Hydride generation - ICP-OES

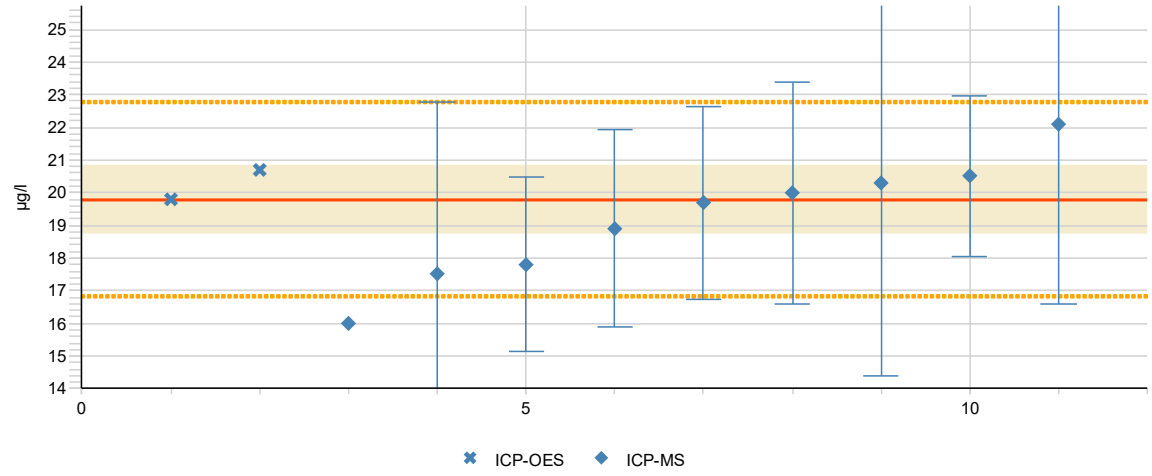

Measurand Se Sample P2M
µg/l
49
45
41
37
33
29
25
21
0
5
10
ICP-OES
ICP-MS


Measurand Se Sample TN3
µg/l
19
18
17
16
15
14
13
12
11
10
9
8
0
5
10
ICP-OES
ICP-MS
Hydride generation - ICP-OES

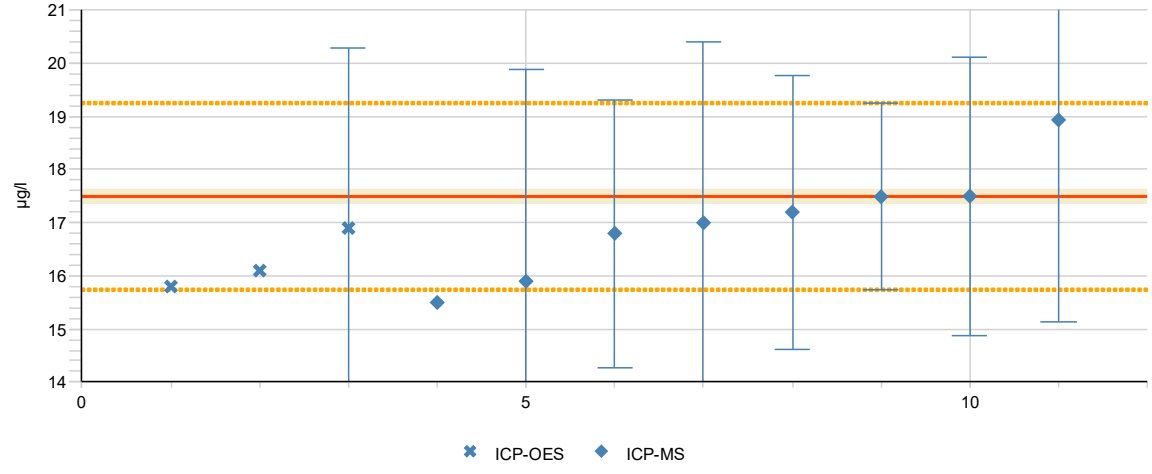
Measurand Se Sample TY3

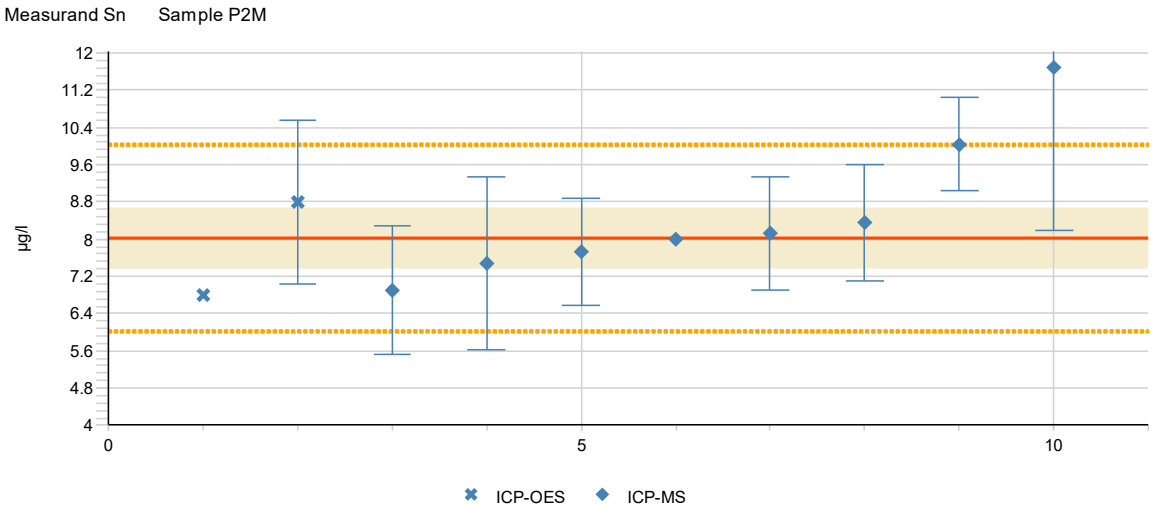


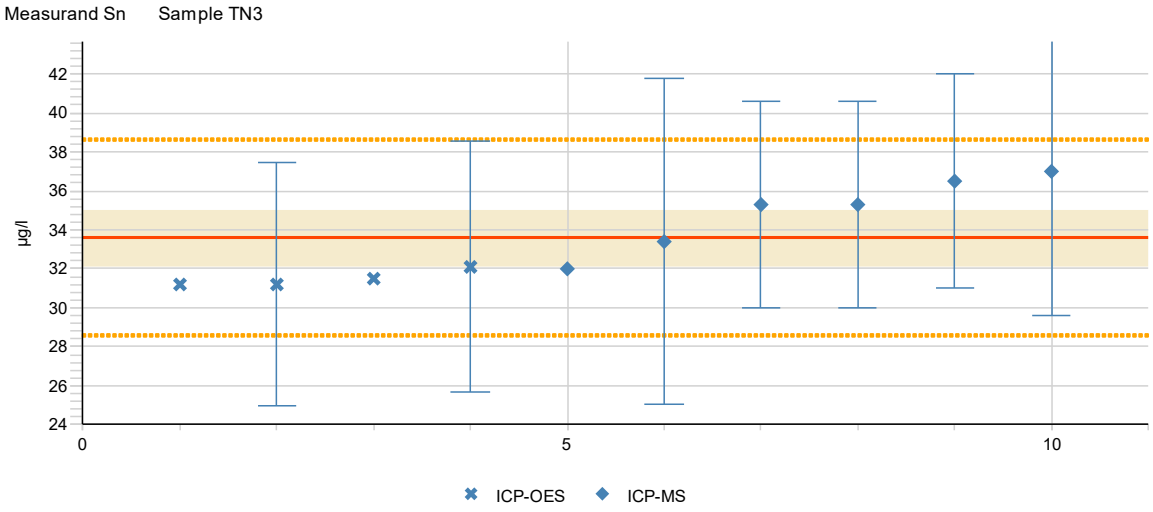
Measurand Se Sample V4M

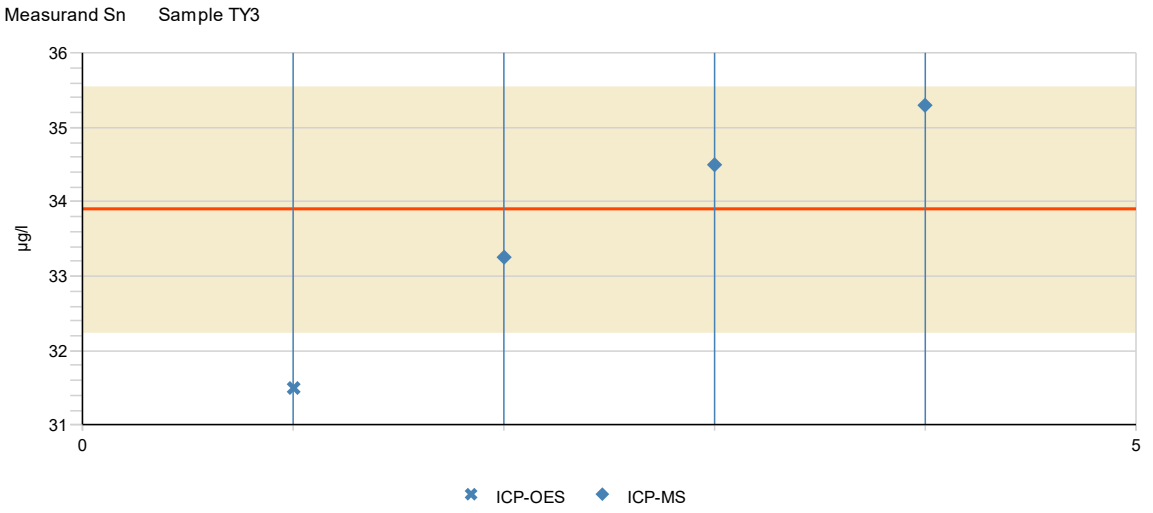


Measurand Sn Sample A1M

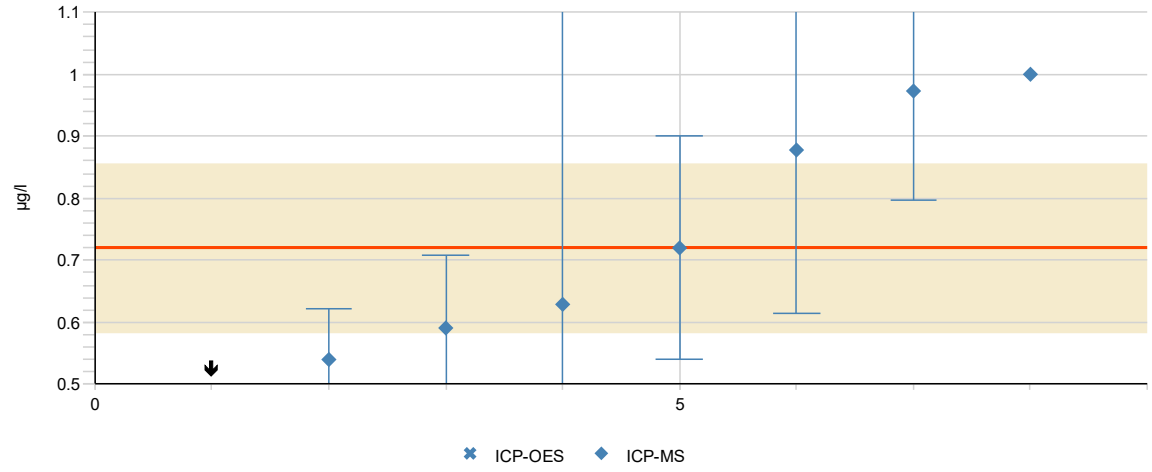



Measurand Sn Sample P2M
µg/l
12
11.2
10.4
9.6
8.8
8
7.2
6.4
5.6
4.8
4
0
5
10
ICP-OES
ICP-MS

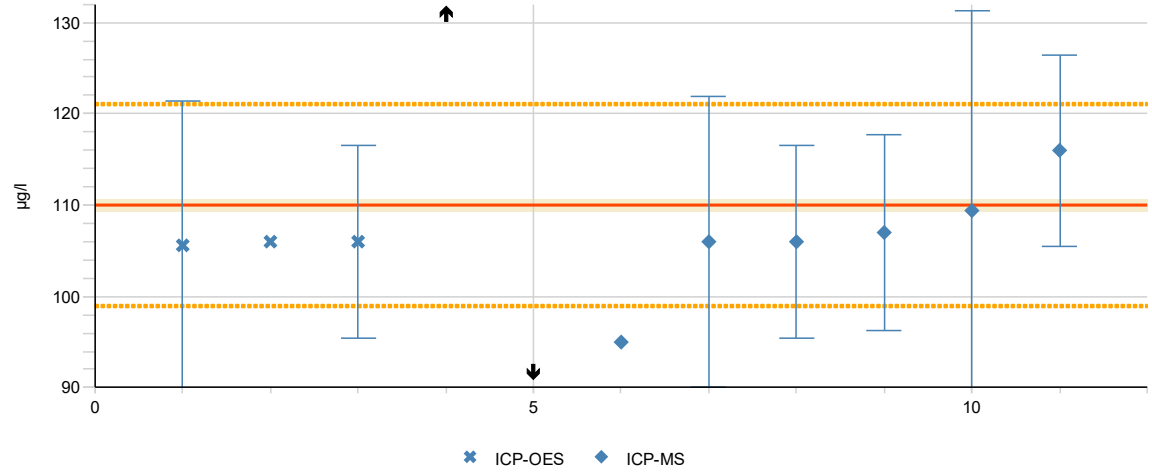

Measurand Sn Sample TN3
µg/l
42
40
38
36
34
32
30
28
26
24
0
5
10
ICP-OES
ICP-MS


Measurand Sn Sample TY3
µg/l
36
35
34
33
32
31
0
5
ICP-OES
ICP-MS

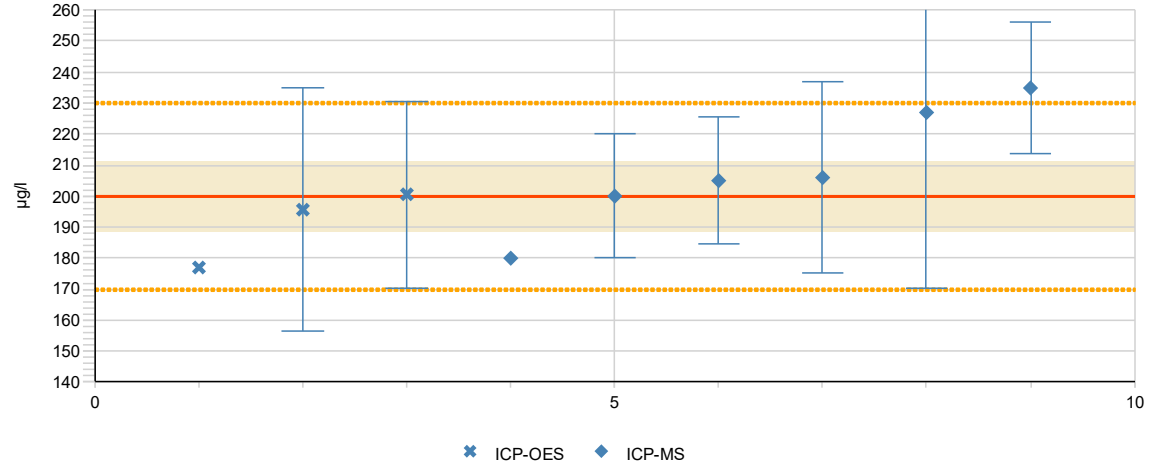
Measurand Sn Sample V4M

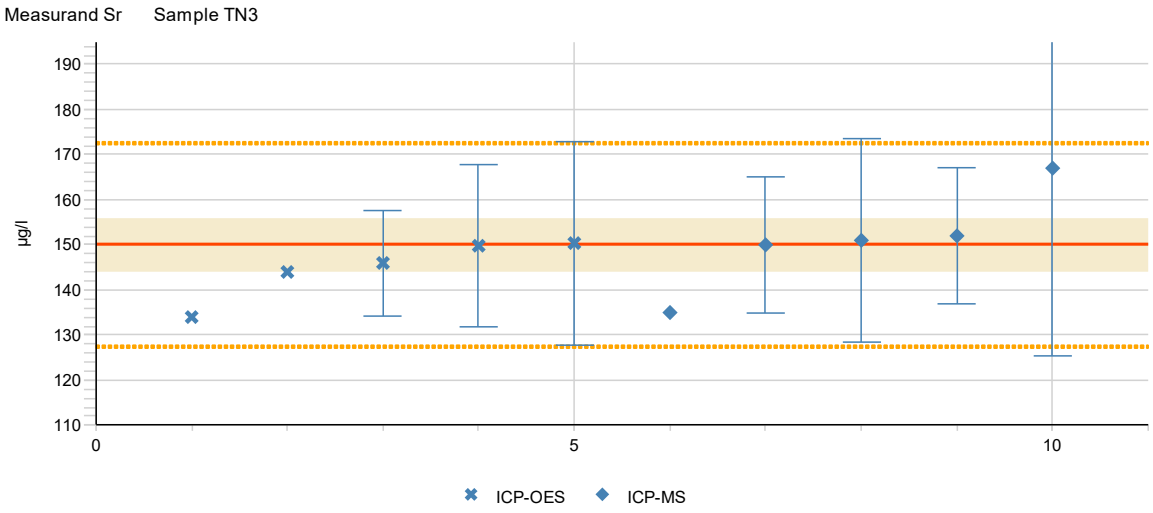


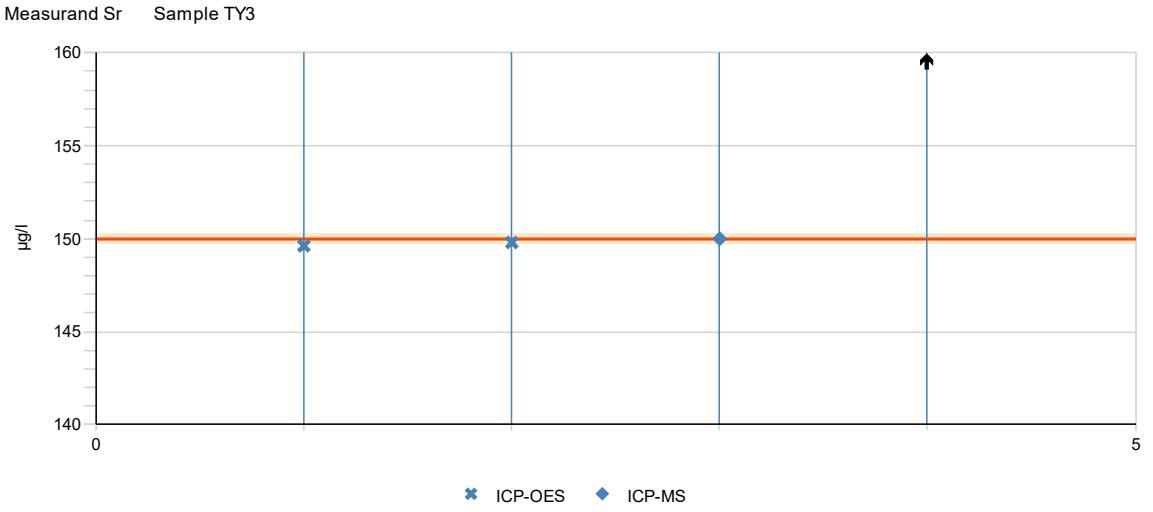
Measurand Sr Sample A1M

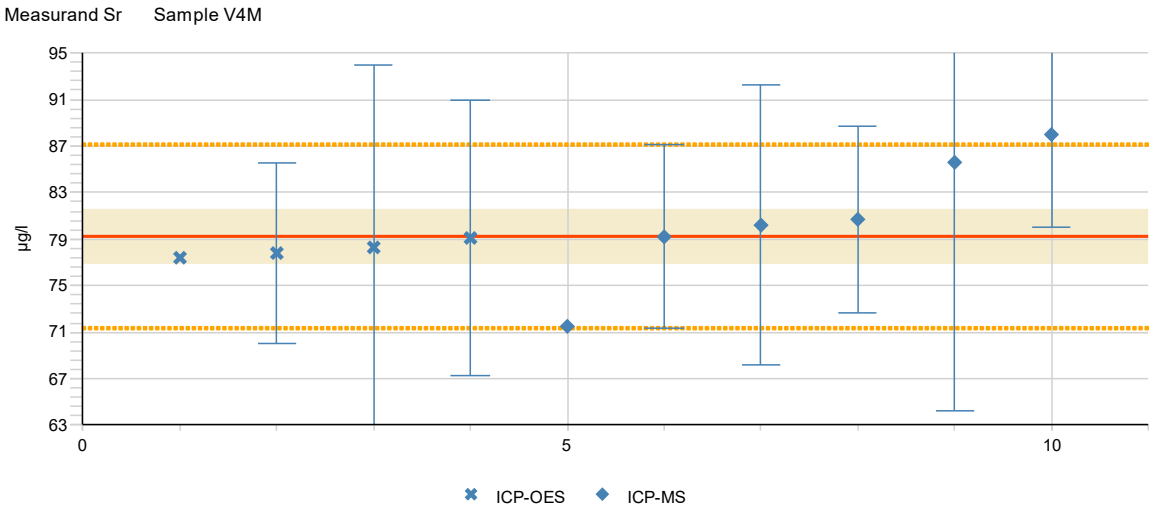


Measurand Sr Sample P2M

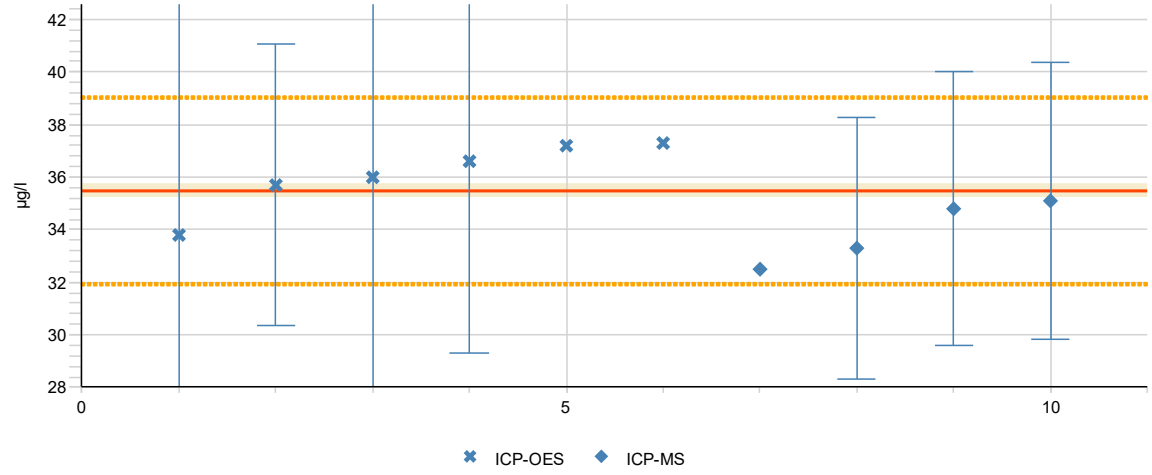



Measurand Sr Sample TN3
µg/l
190
180
170
160
150
140
130
120
110
0
5
10
ICP-OES
ICP-MS

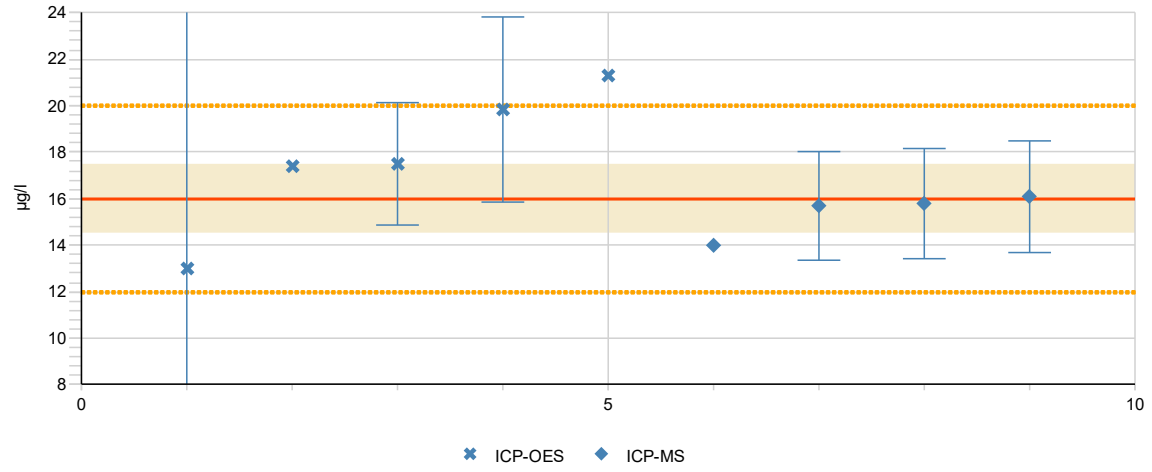

Measurand Sr Sample TY3
µg/l
160
155
150
145
140
0
5
ICP-OES
ICP-MS


Measurand Sr Sample V4M
µg/l
95
91
87
83
79
75
71
67
63
0
5
10
ICP-OES
ICP-MS

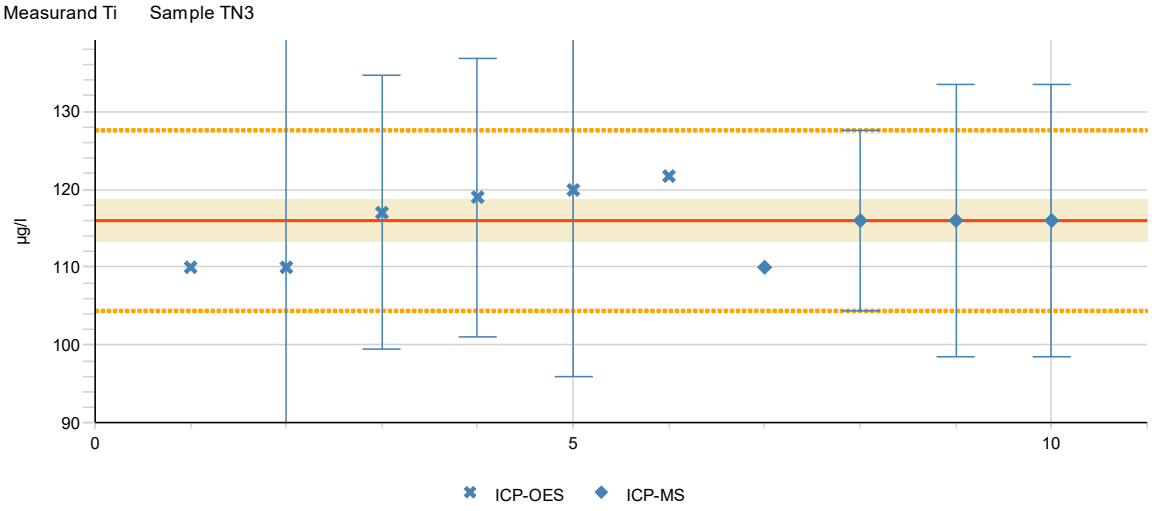
Measurand Ti Sample A1M



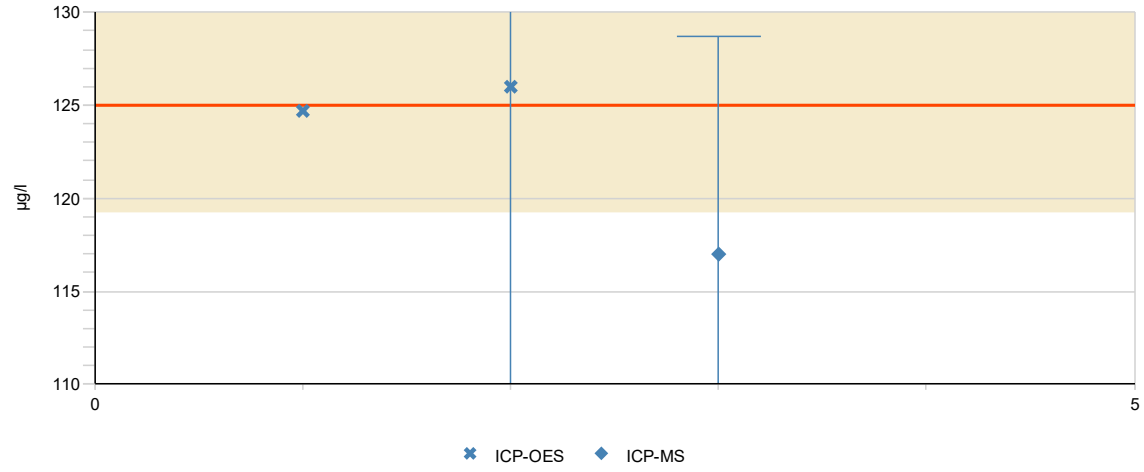
Measurand Ti Sample P2M



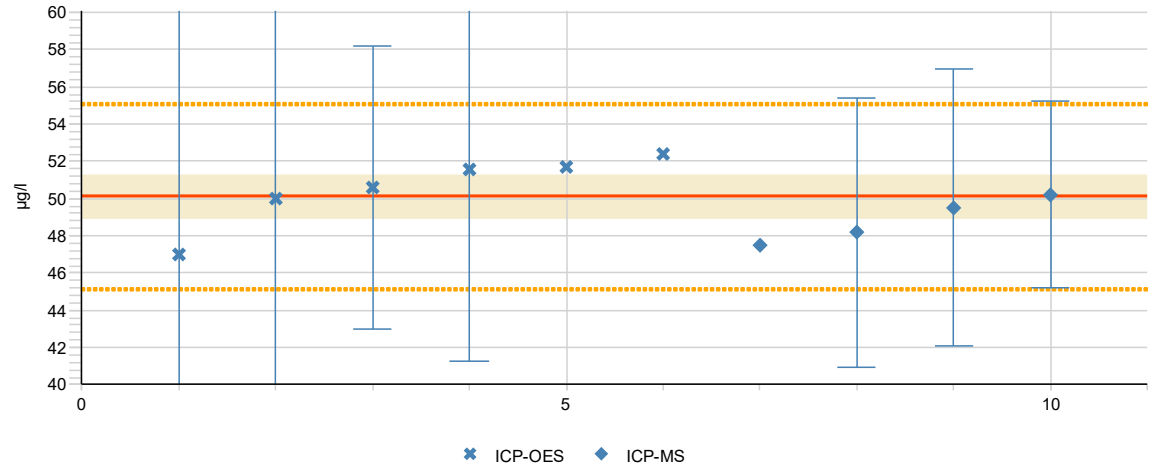
Measurand Ti Sample TN3



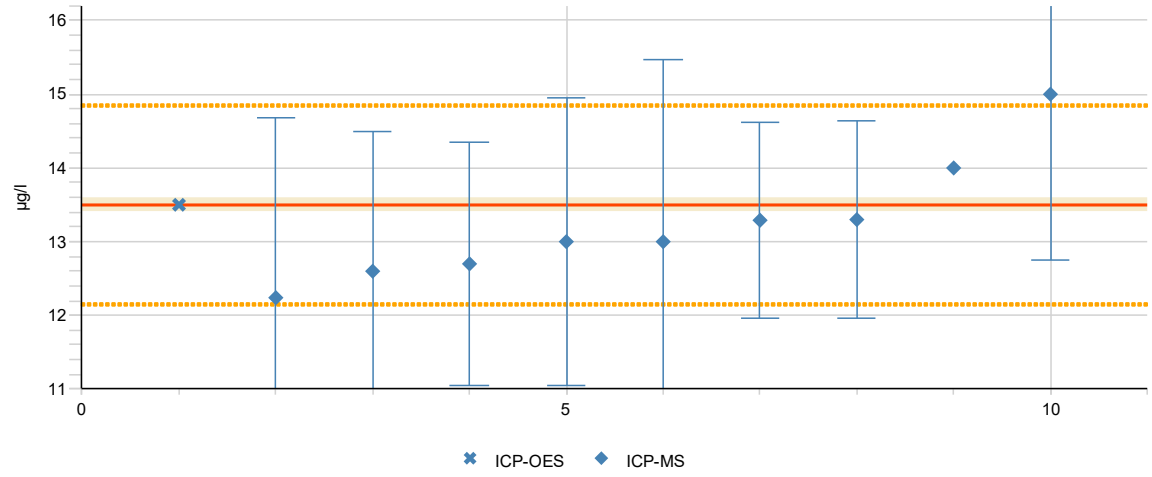
Measurand Ti Sample TY3

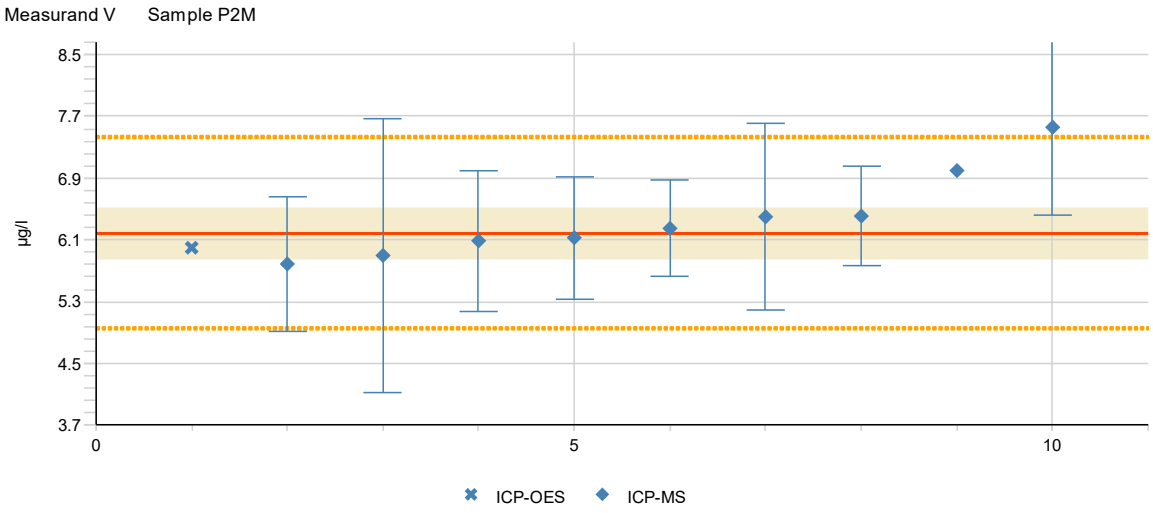


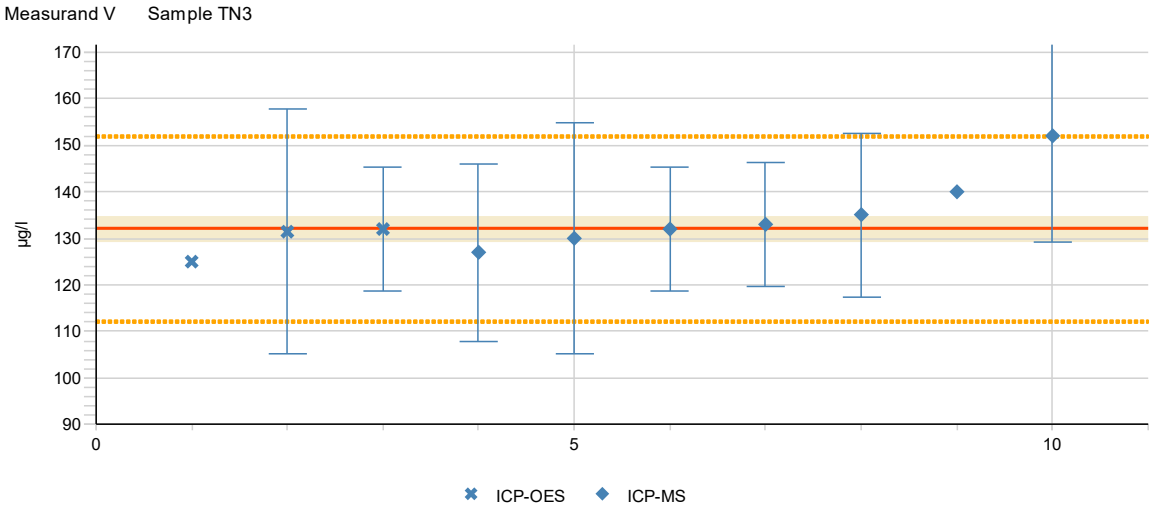
Measurand Ti Sample V4M

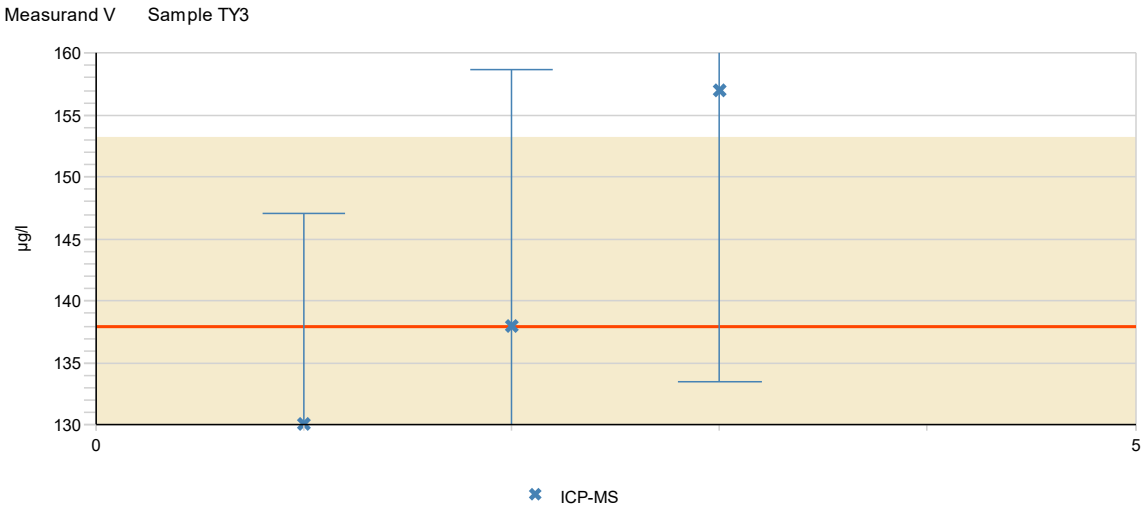


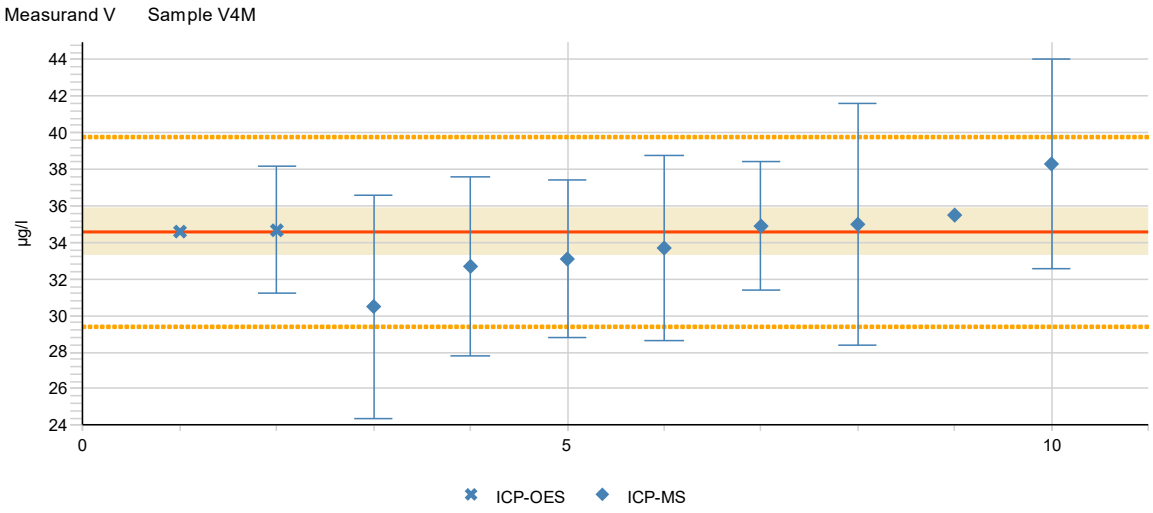
Measurand V Sample A1M

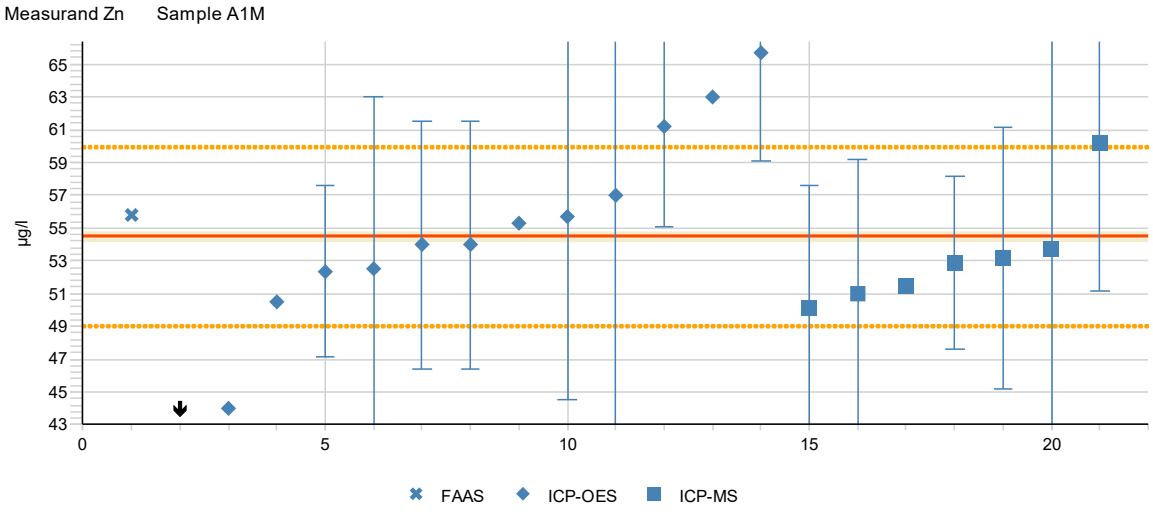


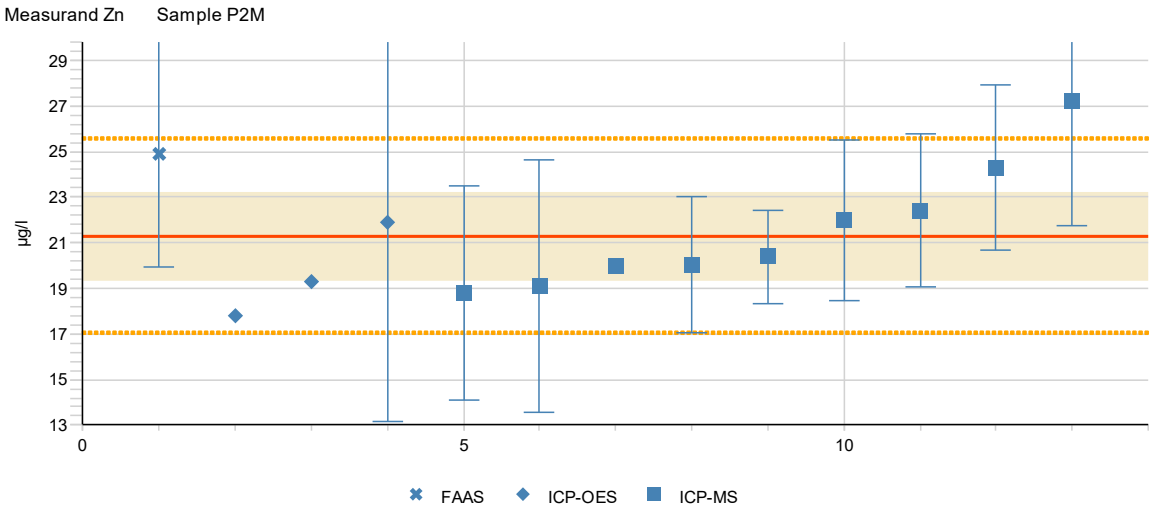

Measurand V Sample P2M
µg/l
8.5
7.7
6.9
6.1
5.3
4.5
3.7
0
5
10
ICP-OES
ICP-MS


Measurand V Sample TN3
µg/l
170
160
150
140
130
120
110
100
90
0
5
10
ICP-OES
ICP-MS

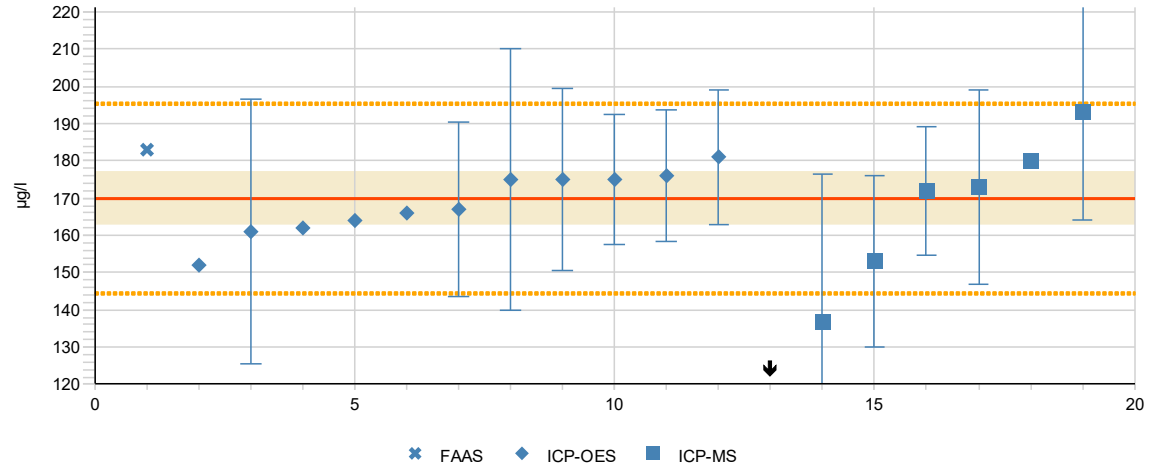

Measurand V Sample TY3
µg/l
160
155
150
145
140
135
130
0
5
ICP-MS


Measurand V Sample V4M
µg/l
44
42
40
38
36
34
32
30
28
26
24
0
5
10
ICP-OES
ICP-MS

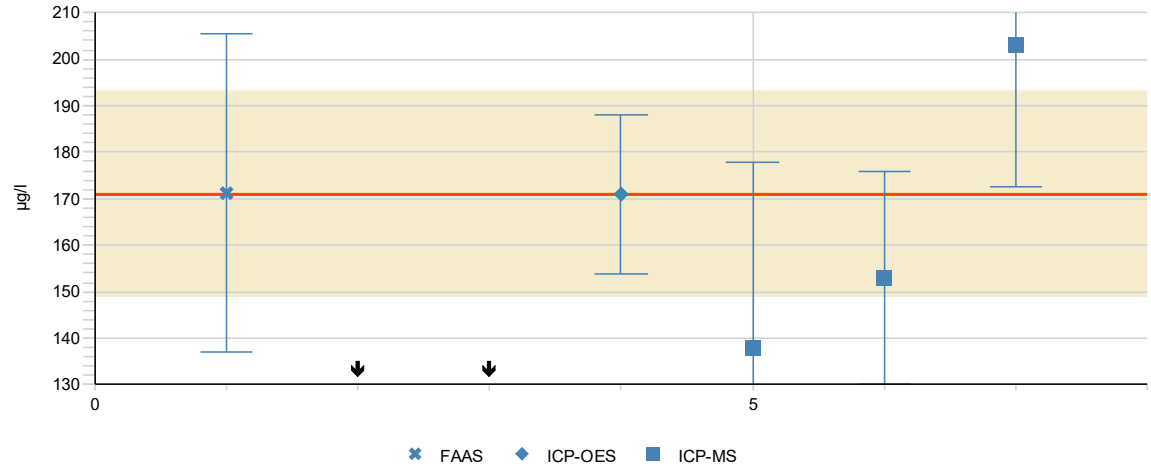

Measurand Zn Sample A1M
µg/l
65
63
61
59
57
55
53
51
49
47
45
43
0
5
10
15
20
FAAS
ICP-OES
ICP-MS


Measurand Zn Sample P2M
µg/l
29
27
25
23
21
19
17
15
13
0
5
10
FAAS
ICP-OES
ICP-MS

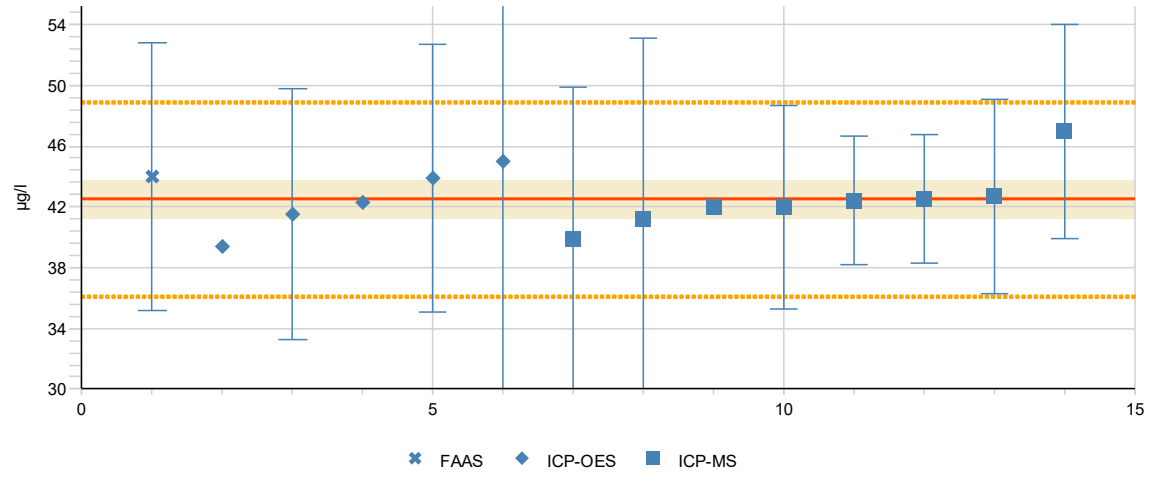
Measurand Zn Sample TN3



Measurand Zn Sample TY3



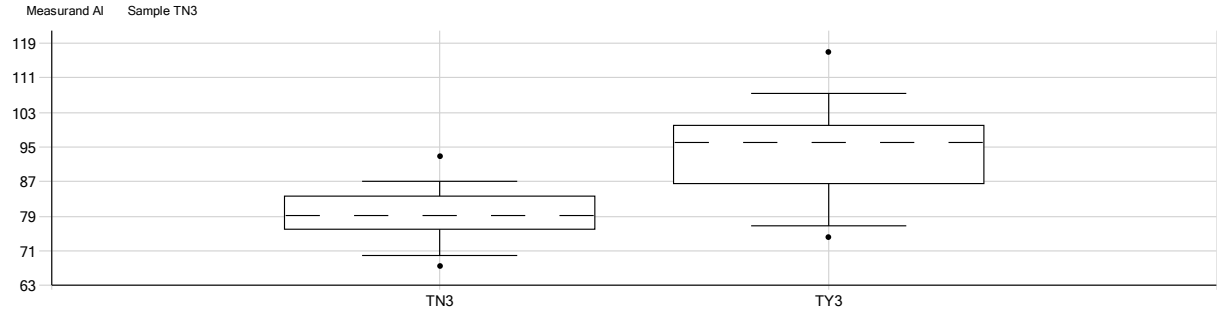
Measurand Zn Sample V4M



APPENDIX 12: Significant differences in the results reported using different methods

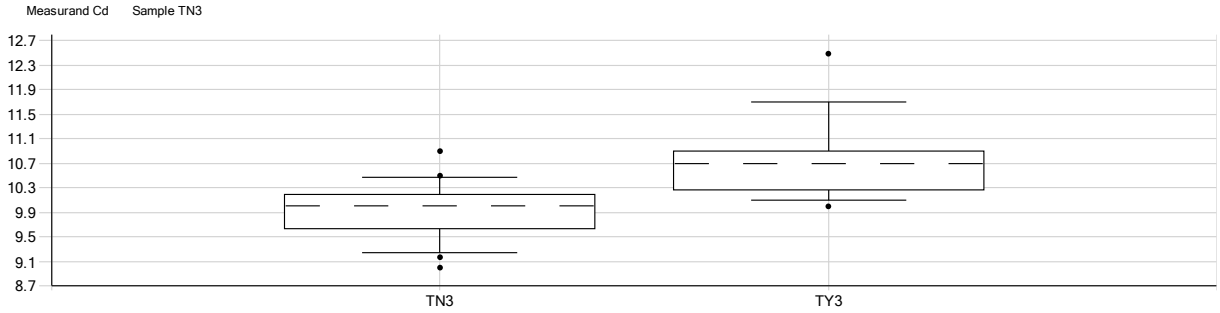
Boxplot figures: In the box the upper and lower limit included 50 % of the results. The dashed vertical line in the middle of the box is the median of the results. The vertical lines above and under the box describe the limits of 80 % of the results. The black dots describe the highest and smallest results within the center 90 % of the results.

Statistically significant differences between pretreatment methods



Method	n	Mean (µg/l)	Median (µg/l)	s (µg/l)
TN3: no digestion	11	79.3	79.2	7.4
TY3: digestion with acid(s)	7	94.4	96.0	14.4

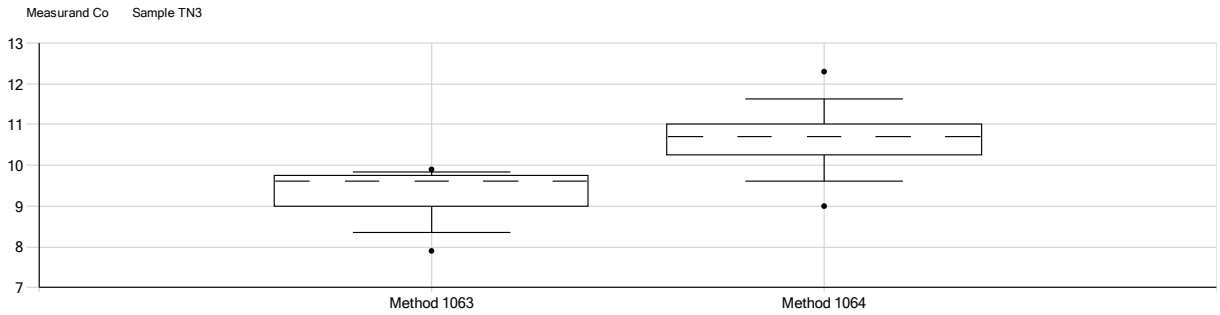
n=number of results; s=standard deviation



Method	n	Mean (µg/l)	Median (µg/l)	s (µg/l)
TN3: no digestion	13	9.96	10.0	0.53
TY3: digestion with acid(s)	6	10.8	10.7	0.89

n=number of results; s=standard deviation

Statistically significant differences between analytical methods

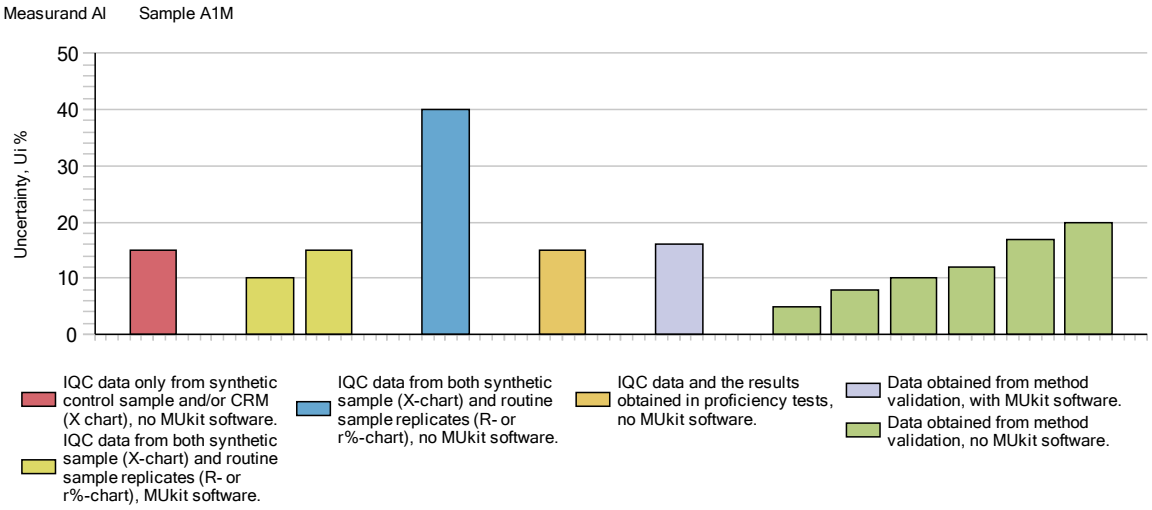


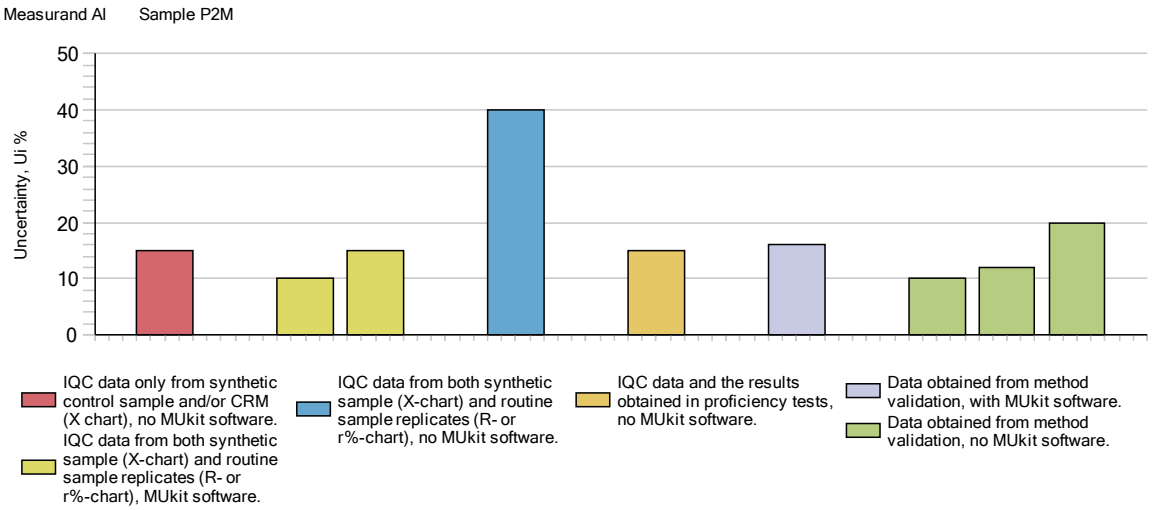
Method	n	Mean (µg/l)	Median (µg/l)	s (µg/l)
1063: ICP-OES	5	9.23	9.60	0.8
1064: ICP-MS	7	10.6	10.7	1.0

n=number of results; s=standard deviation

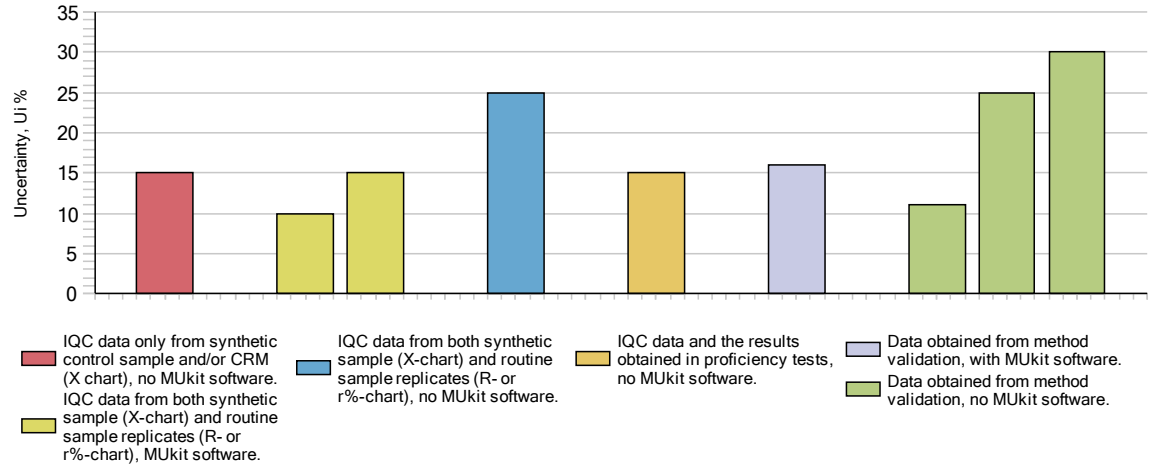
APPENDIX 13: Examples of measurement uncertainties reported by the participants

In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [6, 7].

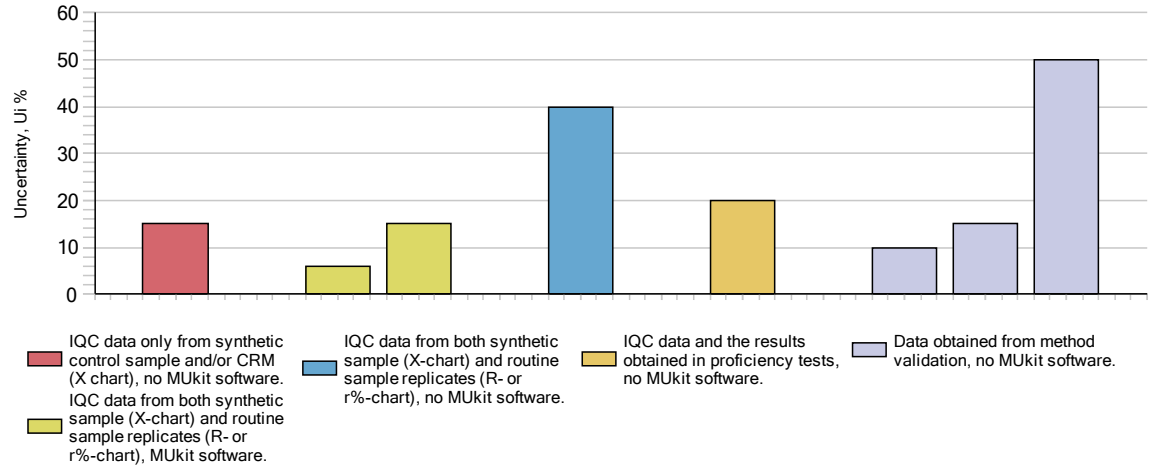




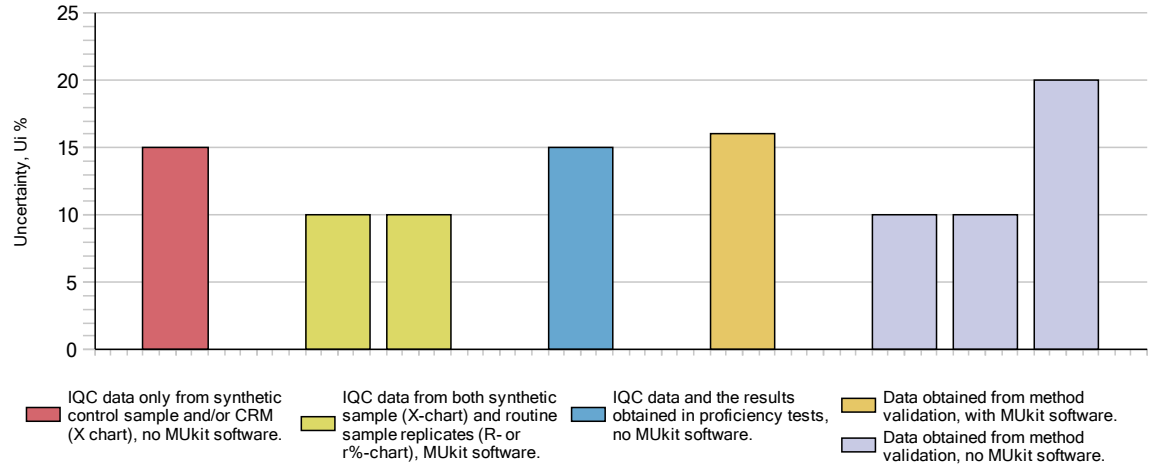
Measurand As Sample V4M



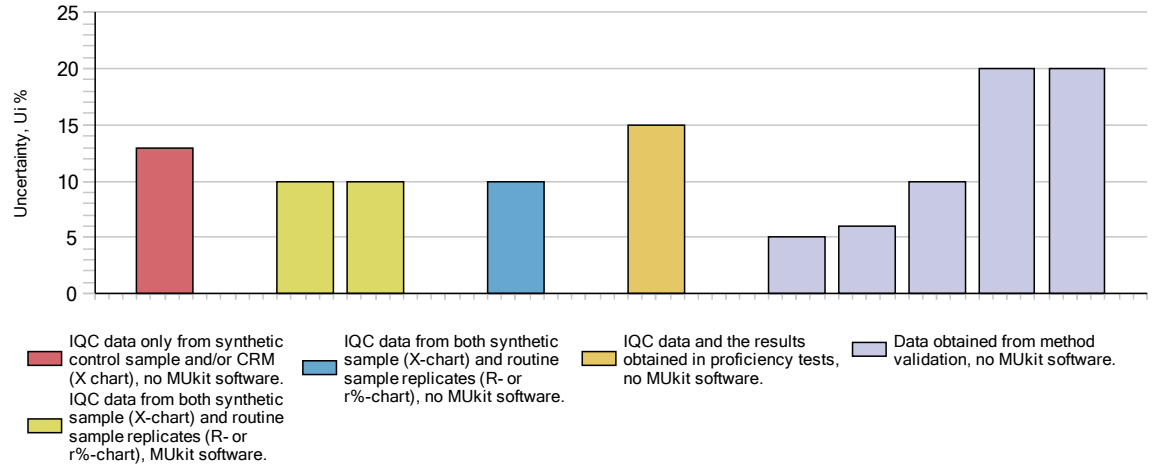
Measurand B Sample TN3



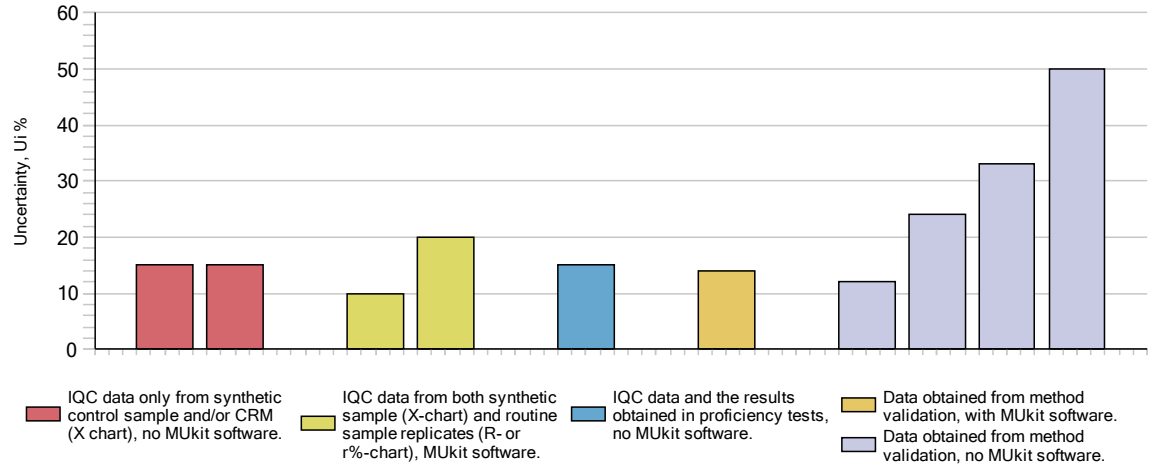
Measurand Ba Sample A1M



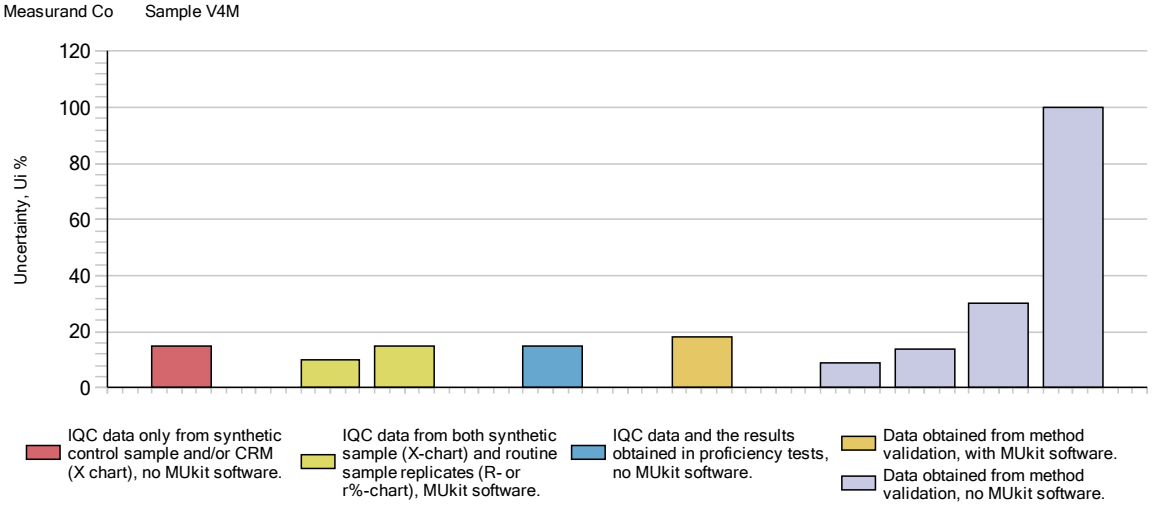
Measurand Ca Sample A1M



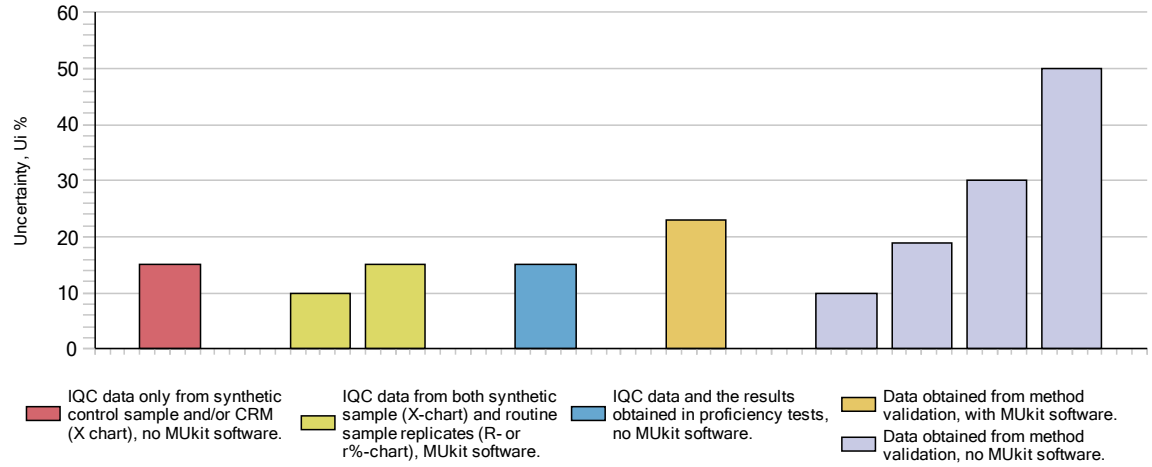
Measurand Cd Sample TN3



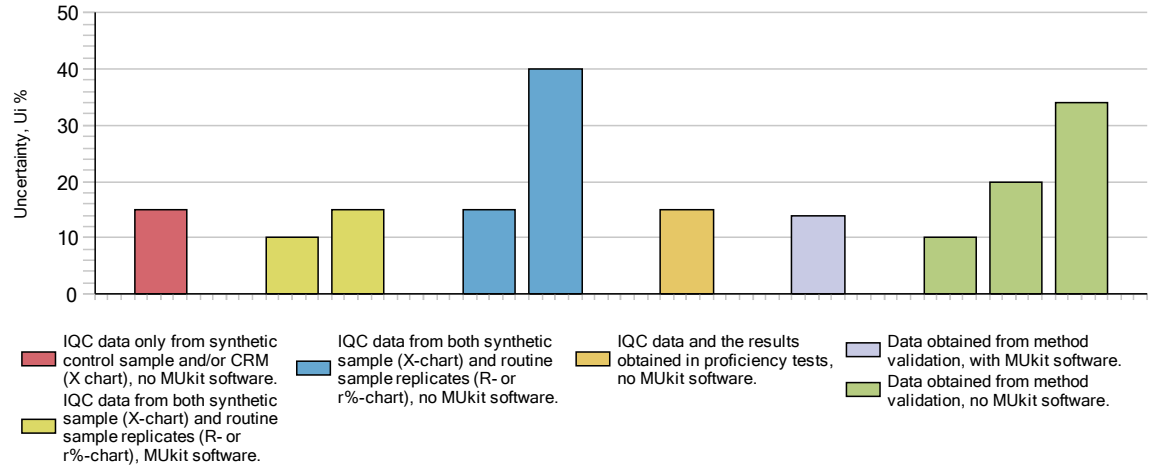
Measurand Co Sample V4M



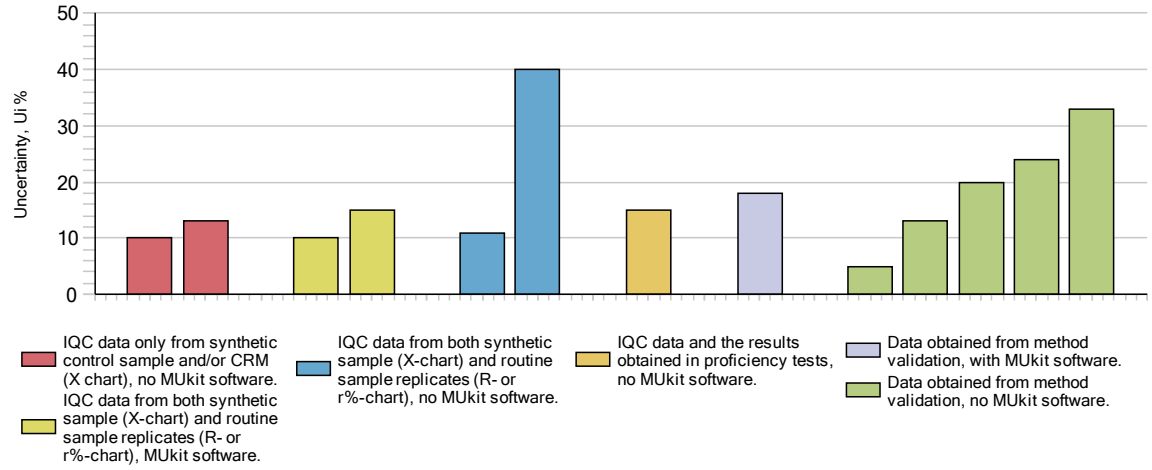
Measurand Cr Sample V4M



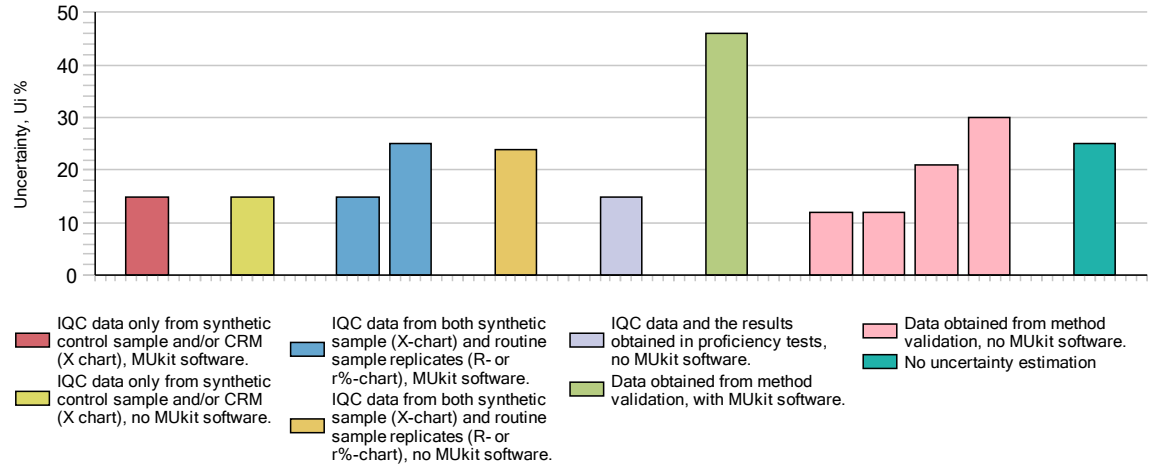
Measurand Cu Sample P2M



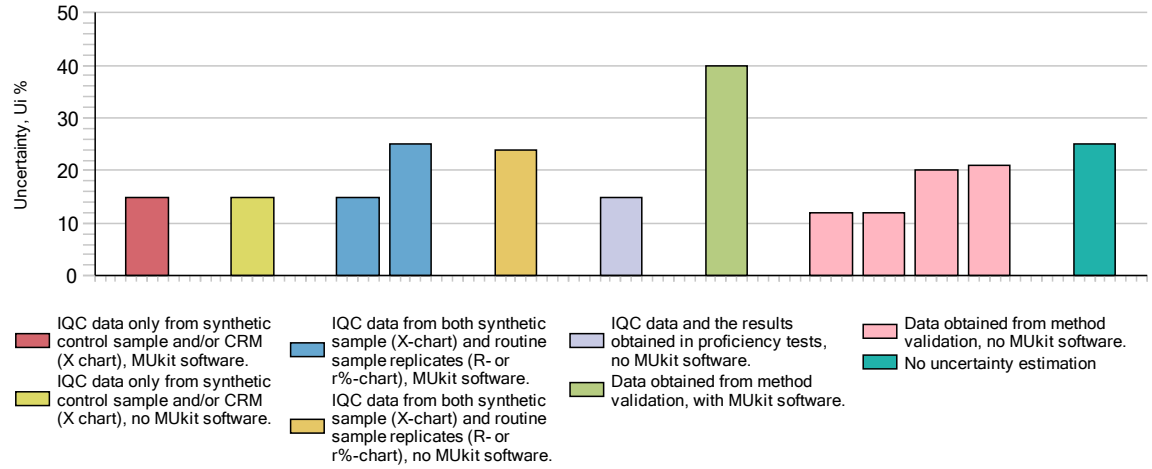
Measurand Fe Sample TN3



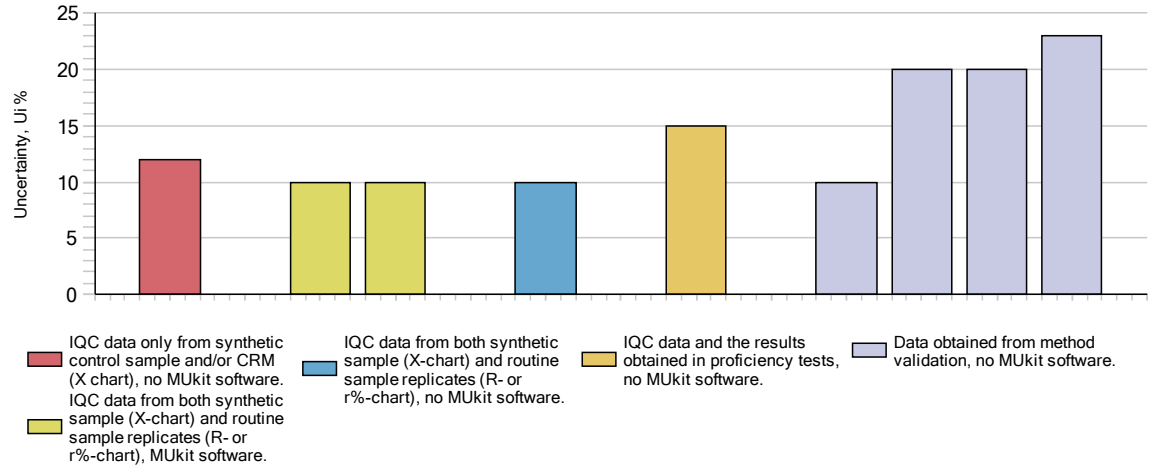
Measurand Hg Sample A1Hg



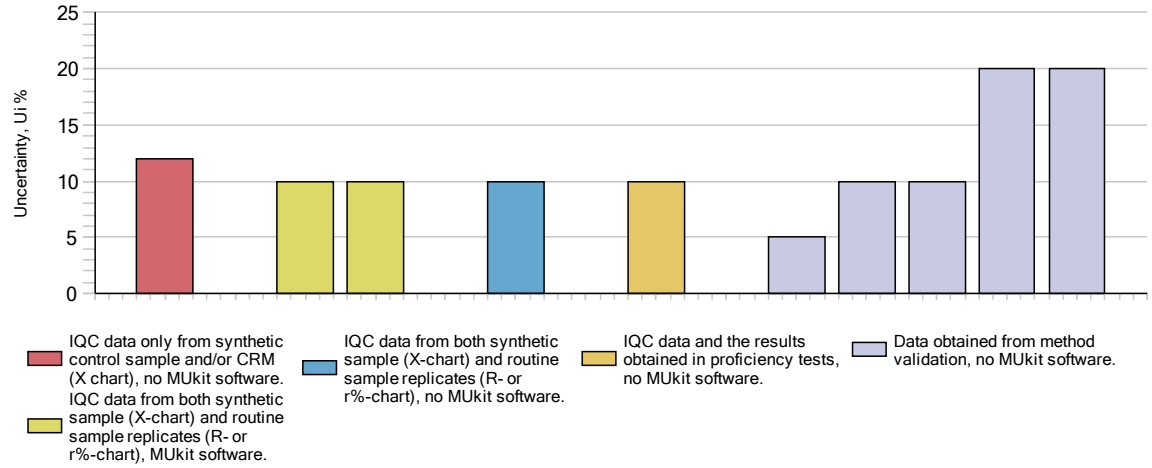
Measurand Hg Sample T3Hg



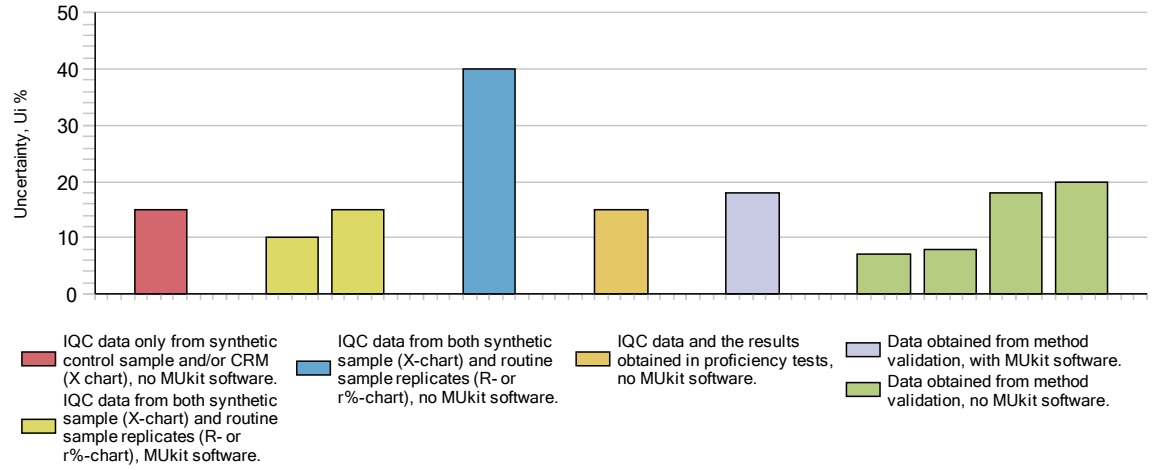
Measurand K Sample P2M



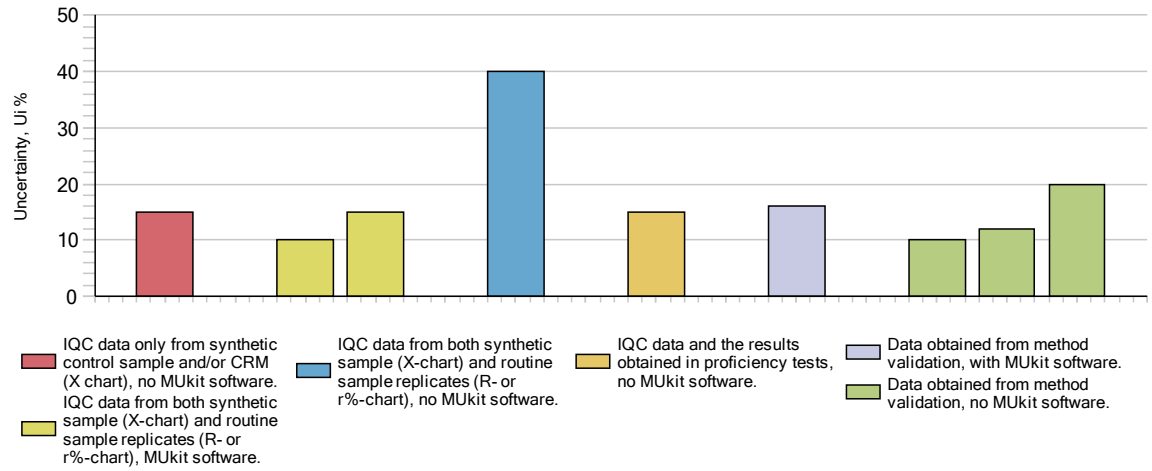
Measurand Mg Sample V4M



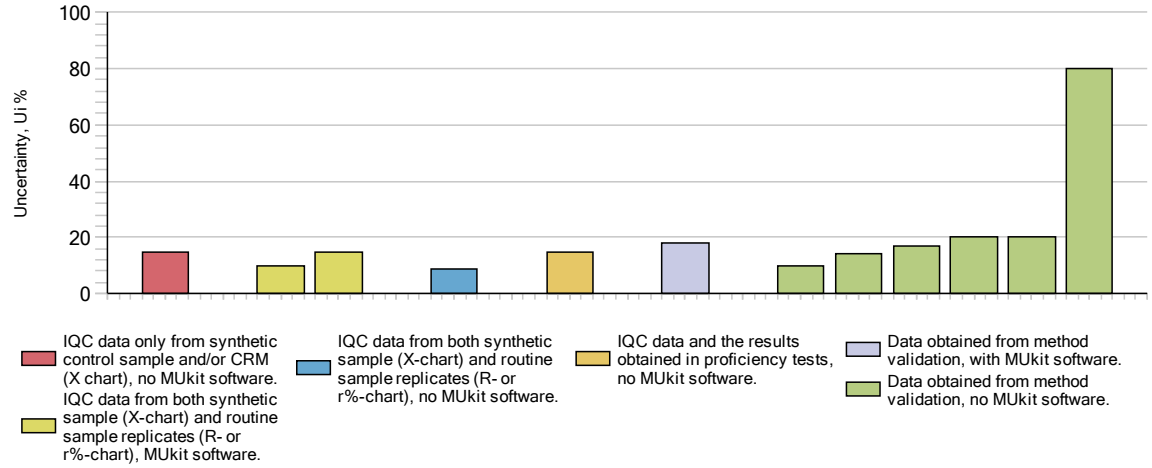
Measurand Mn Sample V4M



Measurand Mo Sample P2M

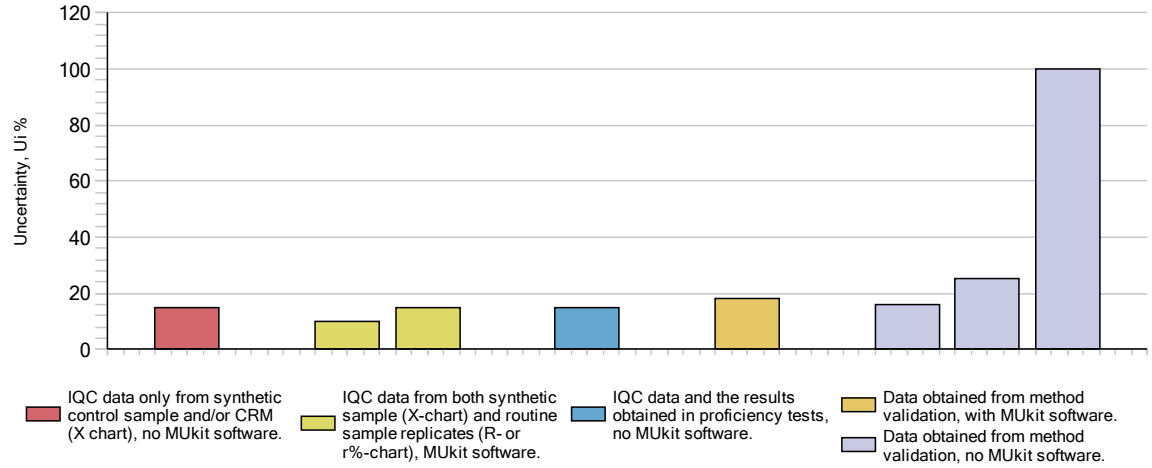


Measurand Ni Sample A1M



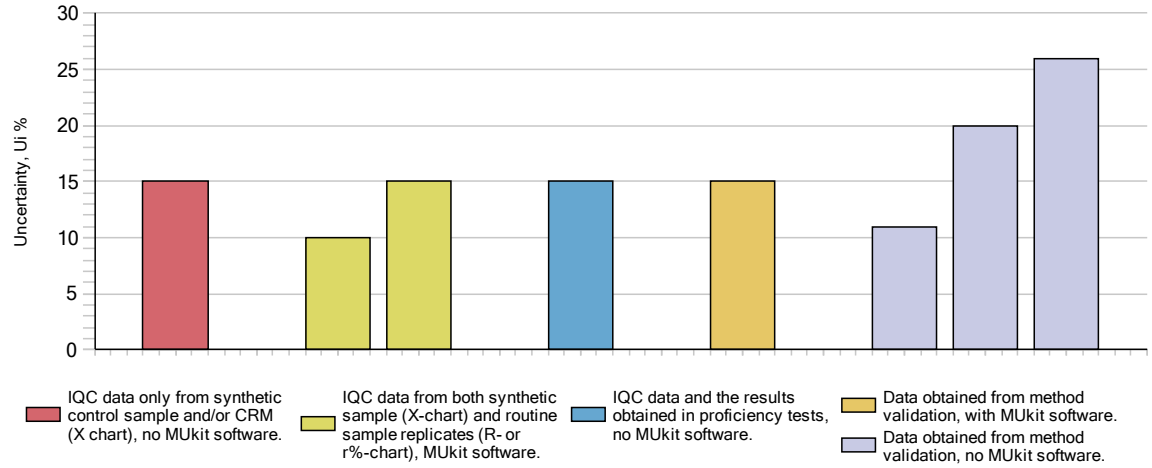
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
Data obtained from method validation, no MUkit software.

Measurand Pb Sample TN3



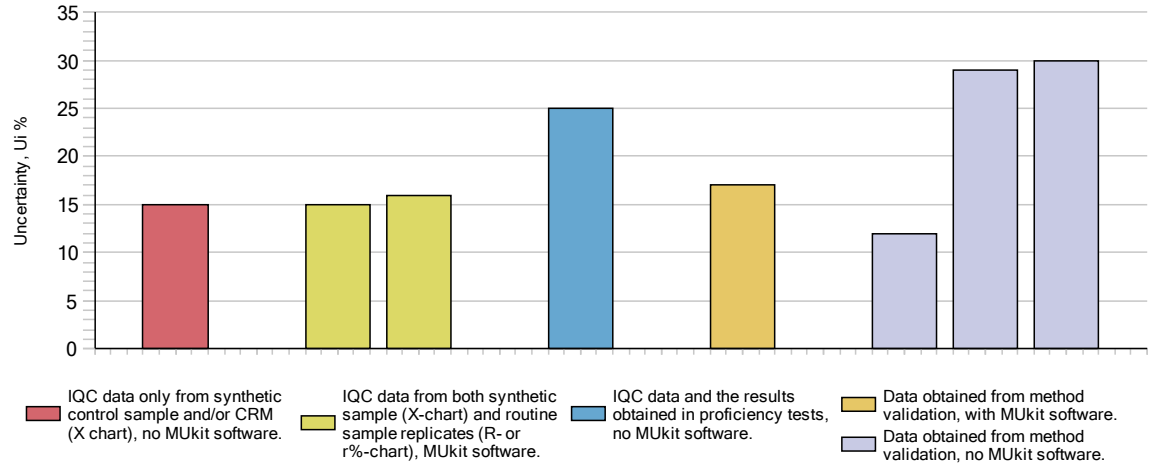
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.

Measurand Sb Sample P2M

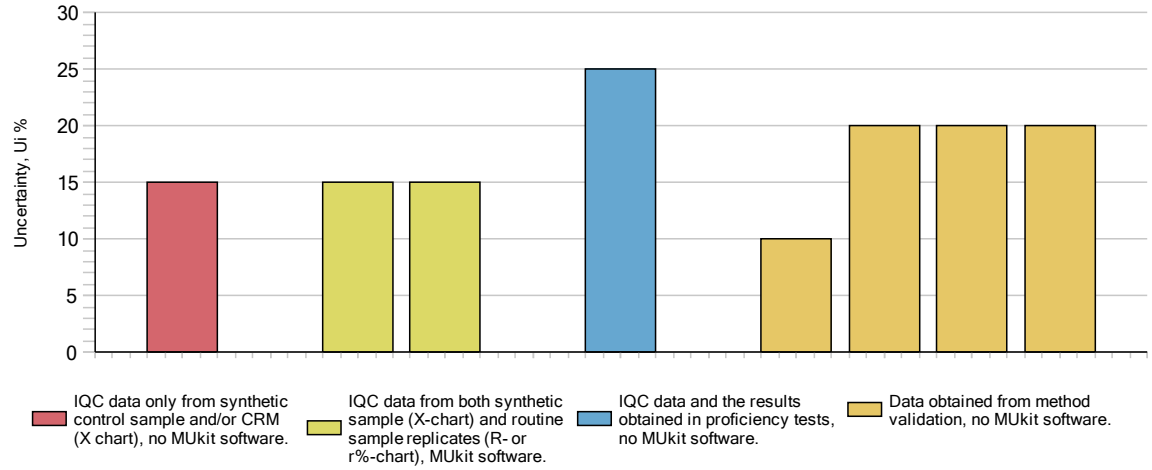


IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.

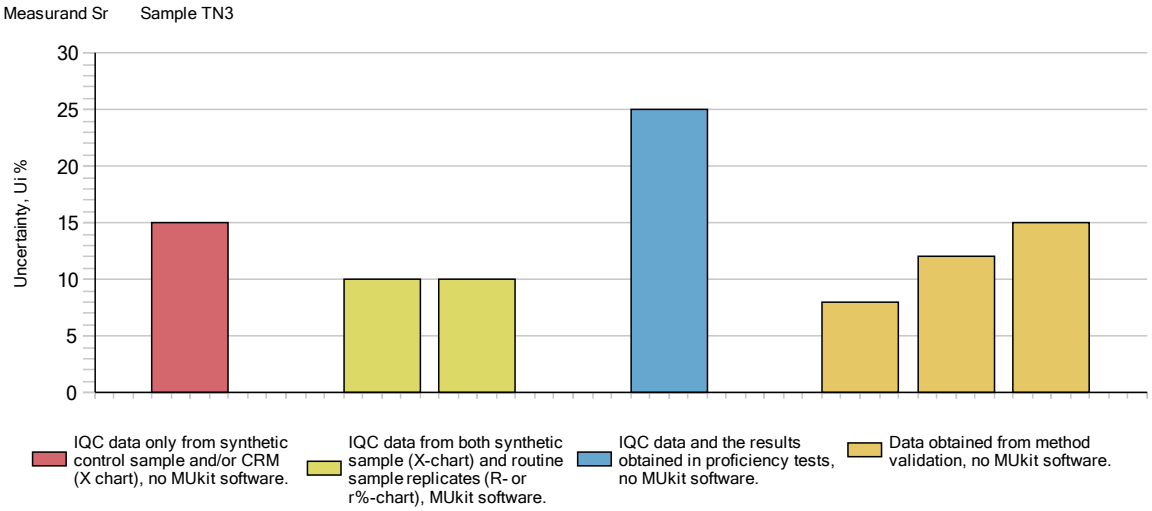
Measurand Se Sample V4M



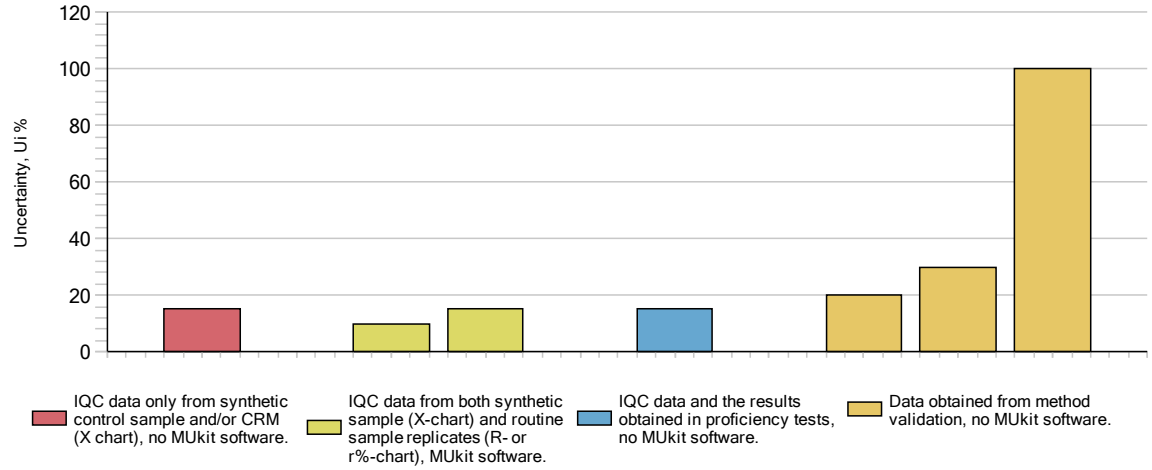
Measurand Sn Sample A1M



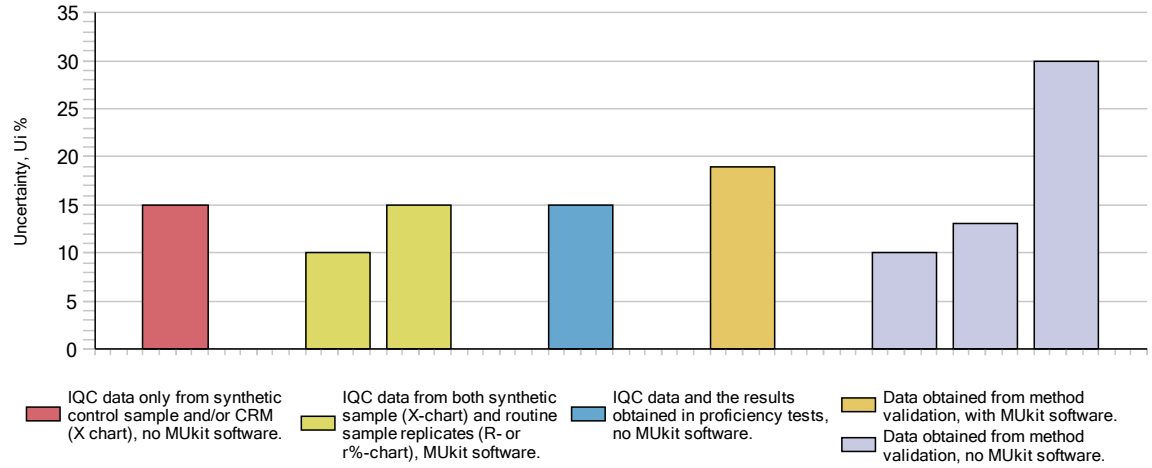
Measurand Sr Sample TN3



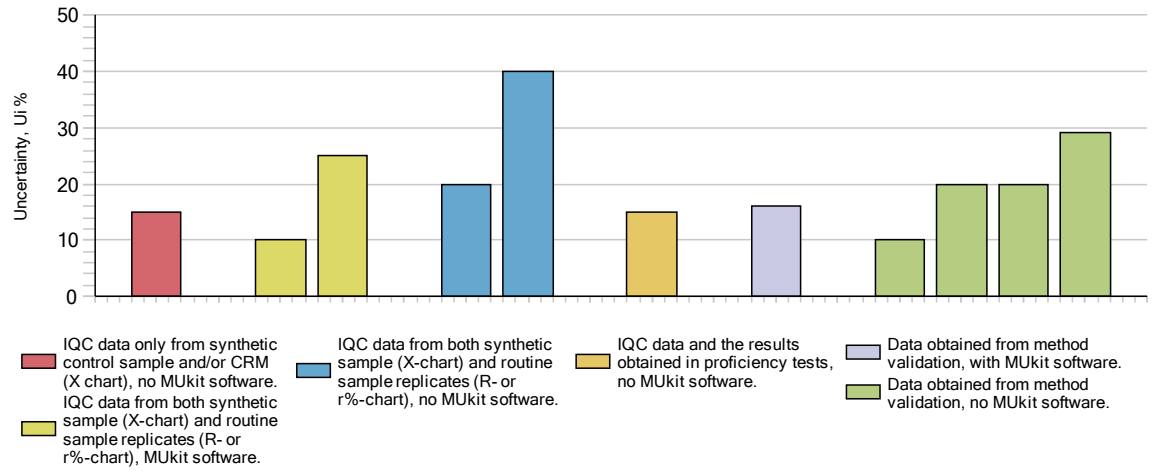
Measurand Ti Sample V4M



Measurand V Sample P2M



Measurand Zn Sample V4M



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